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"RADIOLYSIS OF DIETHYL ETHER"

by

MARK K.M. NG

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

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FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "RADIOLYSIS OF DIETHYL ETHER", submitted by MARK K.M. NG in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

The γ -induced decomposition of ethyl ether, in the liquid phase and in the gas phase, were investigated.

In the pure liquid ether radiolysis, the major products were hydrogen ($G_i = 3.70$), 2,3-diethoxybutane ($G = 2.63$), ethanol ($G = 2.13$), ethane ($G = 1.27$), ethylene ($G_i = 1.1$), ethyl vinyl ether ($G = 1.13$), and s-butyl ethyl ether ($G = 0.74$). Only hydrogen and ethylene yields were found to decrease with increasing dose. The decrease of ethylene yield might be the result of radical scavenging and secondary reactions with some products whereas the decrease in hydrogen yield might be due to free ion scavenging as well. Binary solutions of ether with ethyl vinyl ether, benzene, and 1,3-pentadiene were also investigated. 1,3-pentadiene was the most effective inhibitor for all the products. Benzene appeared to protect mainly by an activation transfer process, whereas radical scavenging was also operative in the case of ethyl vinyl ether and 1,3-pentadiene. The formation of the major products could be accounted for by a mechanism involving free radicals.

In the gas phase radiolysis, the major radiolytic products were hydrogen ($G = 6.44$), 2,3-diethoxybutane ($G = 2.38$), ethylene ($G = 2.10$), acetaldehyde ($G = 1.4$), methane ($G = 1.26$), ethyl i-propyl ether ($G = 1.0$), formaldehyde ($G = 0.9$), and s-butyl ethyl ether ($G = 0.83$). These values were the same at the doses 1, 2, and 3.5×10^{20} ev/gm. The ether molecules decompose into smaller fragments in the gas phase than in the liquid. The change in product distribution due to the change of phase also reflects the presence of "cage effect" in the liquid phase.

In both phases, the probability of bond cleavage, per bond, is higher in the case of C-O bond than the others.

Deuterated ether radiolysis showed that the methylene group was much more important than the methyl group for hydrogen production. An overall isotope effect of 2.0 was obtained for hydrogen formation.

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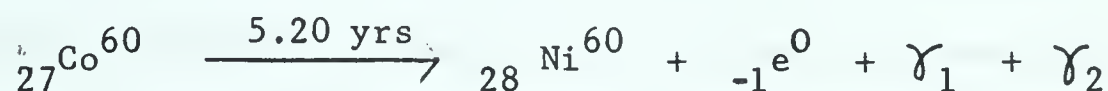
SECTION I - INTRODUCTION

(A) RADIATION CHEMISTRY

(a) General

Radiation chemistry is the study of chemical effects of ionizing radiation on matter. The radiations used are high energy particles and photons — α and β particles, fast neutrons, protons, deuterons, X-rays, γ -rays, etc. They contain energy ranging from a few thousands to many millions of electron volts.

Cobalt-60 γ -rays were used in the present study. Co^{60} decays with a half-life of 5.20 years, emitting β -rays (maximum energy = 0.31 Mev) and two γ -rays (1.17 and 1.33 Mev) (1):



Due to the difference in penetrating powers of β - and γ -rays, the former can be completely shielded, with the proper material, without the latter being affected. The γ -ray photons can be considered as mono-energetic, having an average energy of 1.25 Mev.

Since the photon energy far exceeds the ionization potential of a molecule (10-20ev), both excitation and ionization of molecules can occur in the material irradiated. The electrons ejected from the molecules cause further excitation and ionization.

The final products of radiolysis are formed from the reactions of the activated species (excited molecules, free radicals, and ions). Measurement of the yields of these products will aid in the determination

of the reaction mechanism.

Discussions of the transfer of energy from photons to molecules, reaction mechanisms, the effects of change of phase from liquid to gas, the effects of additives, and isotope effects will be given in (b), (c), (d), (e), and (f) respectively.

(b) Energy Transfer from γ -ray Photons to Molecules

A photon can impart energy to a molecule in several ways (2) (3). Three of the more important ones are considered here.

(1) Photoelectric Effect

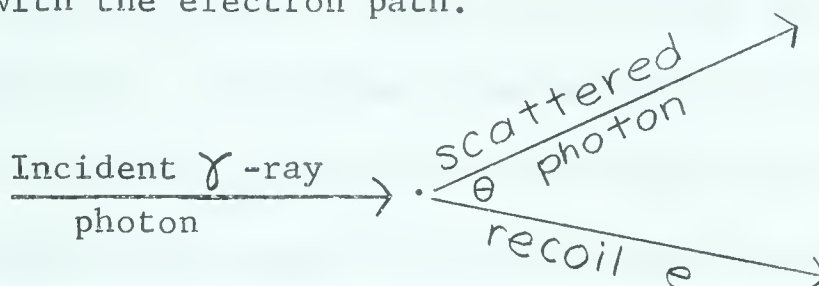
This is a process by which a photon transfers all its energy to an extranuclear electron. Part of the energy is used to overcome the energy binding the electron to the molecule and part of it appears as the kinetic energy of the ejected electron. It is found experimentally that the atomic photoelectric absorption coefficient is proportional to the fourth power of Z , the atomic number. This process is most important for photons of low energy (< 0.5 Mev).

(2) Pair Production

An electron-positron pair is formed by the interaction of the photon with the electromagnetic field of the nucleus. Since the rest mass of an electron contains 0.51 Mev of energy, it requires a minimum of photon energy of 1.02 Mev for pair production. The atomic absorption coefficient for this process is proportional to Z^2 , and its significance increases with increasing photon energy.

(3) Compton Process

When a photon interacts with a free or loosely-bound electron, part of the photon energy is transferred to the recoil electron, known as the Compton electron. The scattered photon emerges with reduced energy, making an angle θ with the electron path.



The atomic absorption coefficient is proportional to Z . The process is the main cause of energy loss when the energy of the γ -rays is around 1 Mev, and the atomic weight of the material irradiated is low.

(c) Reaction Mechanism

The radiolysis of an organic compound results in the formation of excited molecules and ions:



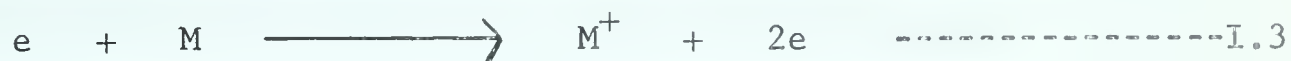
But the subsequent reactions that lead to the formation of final products are still uncertain. As early as 1936, Eyring, Hirschfelder and Taylor (EHT) (4) had satisfactorily interpreted the observed rates of radiation-induced ortho-para hydrogen conversion in terms of reaction kinetics. A tremendous amount of research has been done in radiation chemistry since then. The EHT mechanism was found inadequate to explain new experimental data and hence, was gradually modified (5)(6)(7)(8)(9).

Recently, the study of gas phase radiolysis in mass-spectrometers (10)(11)(12)(13)(14) has given important information about radiochemical processes, especially regarding ion-molecule reactions. The occurrence of free radical reactions is frequently inferred by analogy with photolytic and pyrolytic systems. Much less is known about the liquid phase than gas phase radiolysis. Therefore, frequently, reactions that occur in the gas phase are assumed to take place in the liquid phase when direct evidence in the liquid phase cannot be obtained (see section d).

Brief discussions of possible mechanisms will be given.

(1) The Fate of the Electron

(i) Secondary Ionization



M may or may not be equal to A.

(ii) Secondary Excitation



(iii) Combination with a Positive Ion to form an Excited Molecule



(iv) Attachment to a Neutral Molecule



$M^{\cdot -}$ may dissociate into a free radical and a radical-ion, or it may undergo characteristic reactions with positive ions.

The Compton electrons, which are formed by the interaction of electrons with Co^{60} γ -rays through the Compton process, have a maximum energy of about 1 Mev. Their interactions with molecules result in excitation and ionization of the molecules (reactions I.3 and I.4). Thus, more electrons (secondary) are formed, which in turn cause more ionization and excitation. Since a photon can set in motion, directly as well as indirectly, thousands of electrons, it is these electrons, and not the photons, that are the most important reaction precursors in radiation chemistry.

When the energy of the electrons is reduced below the electronic excitation potential of the molecules, their energy will probably be dissipated in the rotation and vibrational modes of the molecules. However, the ultimate fate of the electrons in most systems is still in question.

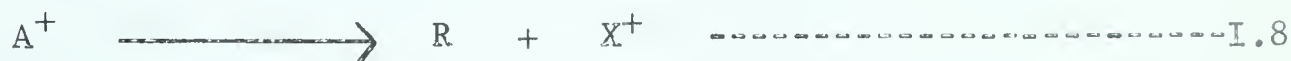
The thermal electron probably combines with a positive ion to form an excited molecule (reaction I.5). The positive ion may or may not be the parent ion. This depends on the ability of the electron to escape the field of the parent ion before it loses its energy. Calculations by Samuel and Magee (15) on water (liquid phase) showed that the electron recombined with the parent ion. However, similar calculations by Platzman (16) showed that the electron escaped from the parent ion. Freeman (17) found that, from conductance measurements of liquid hydrocarbons, the "escaped electrons" had a G-value of about 0.2. Hart and Boag (18) obtained evidence that polarons (or solvated electrons) are precursors to radical species formed in irradiated aqueous systems.

The extent of electron capture by neutral molecules (reaction I.6) is not yet known. Evidence of this reaction was found in several γ -irradiated organic glasses at -190°C (19). Burton and Lispky (20) speculated that one of the protection effects of additives may be due to negative ion formation. In order that reaction (6) can compete favourably with reaction (5), the neutral molecule must have a high electron affinity.

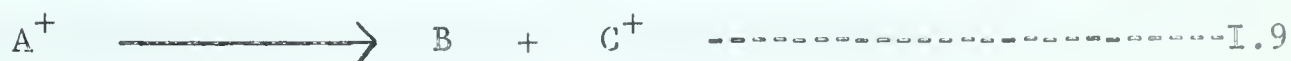
(2) The Fate of the Positive Ion

(i) Combination with an Electron (reaction I.3)

(ii) Dissociation into a Free Radical and a Radical-ion



(iii) Dissociation into a Stable Molecule and a Positive Ion



(iv) Charge Transfer



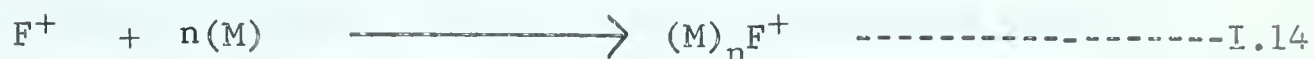
(v) Proton Transfer



HR^+ is equal to A^+ and H is a hydrogen atom.

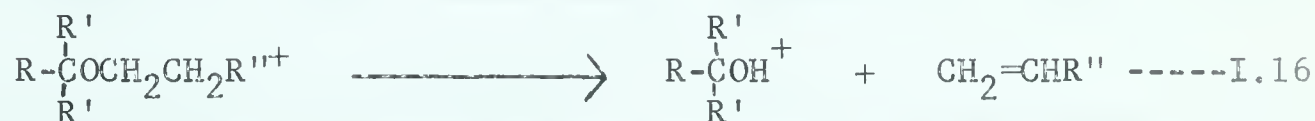
(vi) Hydride-ion Transfer(vii) Combination with a Neutral Molecule

MA^+ may dissociate in subsequent reactions.

(viii) Cationic Polymerization

where F^+ may be A^+ or the fragmentation ion of A^+ , and $n = 1, 2, 3 \dots$

Evidence for reactions I.8 and I.9 was observed by McLafferty (21) on the mass spectrometric analysis of aliphatic ethers:

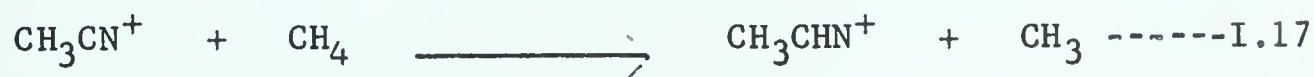


Field (22) observed the unimolecular decomposition of intermediate complex ions in the radiolysis of ethylene at low pressure. At high pressure, and in condensed phase, these reactions will probably be suppressed by other reactions such as ion-molecule reactions and collisional processes.

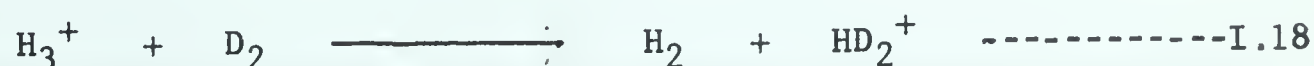
The important role of ion-molecule reactions in radiation chemistry (reactions I.10 to I.15) has been ascertained by mass spectrometric studies (10)(11)(12)(13)(14). These studies showed that ion-molecule reactions were very fast compared to ion-electron recombination under atmospheric pressure. The high probability of ion-molecule reactions was also cited by Williams (23) in the radiolysis of liquid hydrocarbons. The main features of ion-molecule reactions are low activation energy and large reaction cross section.

Reaction I.10 is a resonant charge transfer process (24) when M is equal to A. This process has a large cross section because it does not involve collision. The process takes place when an electron jumps from one molecule to another. This is called the positive hole migration in the condensed phase. Though this hole migration process occurs readily in solid, its existence in liquid is not yet confirmed. The energy transfer mechanism in cyclohexane-benzene and cyclohexane-cyclohexene systems is probably due to hole migration (25)(26). When A is different from M, it becomes a non-resonant quenching process (24).

A good example of hydrogen abstraction by cyanide radical-ion was given by Martin and Melton (27):



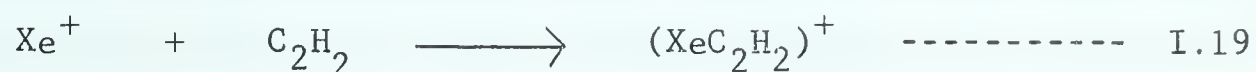
Proton transfer mechanism was observed in the radiation-induced exchange of hydrogen and deuterium by Schaeffer and Thompson (28):



Lampe et al (29) found evidence of hydride-ion transfer in the mass spectrometric investigation of hydrocarbons. Futrell (30) claimed

that hydride-ion transfer was an important reaction in the radiolysis of n-hexane, in both the liquid and gas phases.

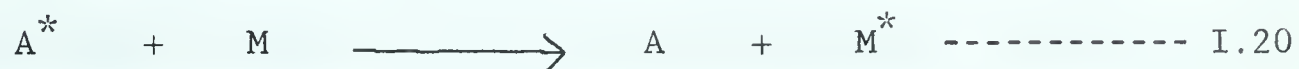
An addition reaction (reaction I.13) was postulated by Melton et al (31) in the radiolysis of Xe-C₂H₂ system:



Cationic polymerization was suggested by Dainton et al (32) to occur in the liquid phase radiolysis of isobutene. (CH₃)₃C⁺ was the most likely chain-initiating ion.

(3) Fate of the Excited Molecule

(i) Energy Transfer



(ii) Rearrangement and Decomposition into Two Stable Molecules



(iii) Decomposition into Radicals



The excited molecules are not confined to the lowest excited state. The superexcited molecules may dissociate into hot radicals or molecules. However, they usually convert quickly to the lowest electronic

state before they react. Conversion from singlet to triplet state also occurs.

Energy migration from an excited molecule to another molecule (reaction I.20) can take place in four different ways (33). One process involves the loss of kinetic energy through a collision of the second kind. In a second process, a photon is emitted by one molecule and is absorbed by another. Thirdly, energy is transferred by a process called inductive resonance, or quantum-mechanical resonance (33). In this process, energy is transferred from a molecule to a distant molecule without the intervening molecules being disturbed. Finally, exciton migration (34) is a process in which the energy jumps from molecules to molecules but does not stay in any of them for over one vibration period. This process is favorable when the molecules are strongly coupled. The theories of inductive resonance and exciton transfer are supported by studies of organic scintillators (35) (36).

Fragmentations of the excited molecules (reaction I.21 and I.22) have been widely studied in pyrolysis and photolysis. Since they are assumed to be analogous in radiolysis, their discussions will be omitted.

(4) The Fate of the Radicals

The radicals will undergo abstraction, combination and disproportionation. In the liquid phase, the back reaction (reaction I.22) of two radicals to form the parent molecule is of considerable importance because of the "cage" effect (see section d).

(d) The Effect of Change of Phase from Gas to Liquid

This effect is mainly due to the relatively larger mean free path in the gas phase. The collision frequency in the gas phase is $\sim 10^{10}$

sec^{-1} at standard temperature and pressure, whereas it is $\sim 10^{13} \text{ sec}^{-1}$ in the liquids.

In gas phase radiolysis, the activated species formed will diffuse rapidly throughout the whole system. The distribution of these species is considered to be homogeneous. Because of its homogeneity, gas phase radiolysis is not likely to be affected by any change in linear energy transfer (LET) (37). Processes such as unimolecular decomposition and radical-radical reactions will probably occur more readily than in liquid phase radiolysis. The electrons ejected from molecules usually escape from the parent ions. Consequently, ion-molecule reactions (38) are highly probable.

In liquid phase radiolysis, the activated species are formed in groups or "spurs" along the tracks of the incident beam of irradiation (37). Thus, it is expected that the distribution of these species is dependent on the change of LET. The radicals formed are considered to be trapped by the surrounding molecules. This "cage" effect (39) increases the probability of their recombination to form the parent molecule. The activated species will probably undergo collisional deactivation more readily than in the gas phase. In the gas phase, the cage effect probably becomes significant only when the pressure of the gas is high (40).

In conclusion, the reaction mechanism of radiolysis is probably quite different in the two phases. Frequently, both phases give products which are qualitatively similar, but vary quantitatively.

(e) Effects of Additives

(1) Chemical Effects

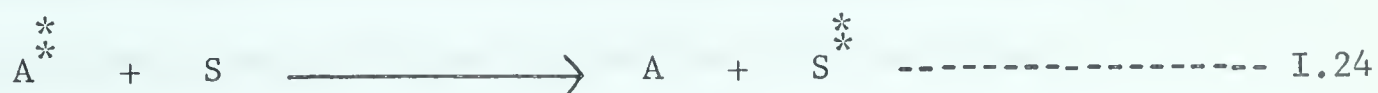
Radicals produced in a pure radiolytic system may undergo reactions that lead to the formation of final products. When a reactive solute is added to the system, the radical-solute reaction will compete with the radical-radical reactions. If the solute concentration is high enough, almost all the radicals will be scavenged by the solute. Thus, the study of the effects of appropriate additives can differentiate radical processes (scavengeable) from molecular processes (unscavengeable). The unscavengeable yields of products are probably formed by unimolecular dissociations, hot radical reactions (41), and, in the liquid phase, radical reactions in the spurs.

(2) Physical Effects

An excited molecule or a positive-ion formed by radiolysis will subsequently react, giving rise to final products P:



where A^{**} refers to either ions or molecules of different states of excitation. In the presence of an additive, the excited molecule or positive-ion may choose to transfer its energy or charge to an additive molecule, S, according to reaction I.24.



If the subsequent reaction of the additive molecule, S^{**} , does not give rise to P (reaction I.25), then the formation of P is said to be inhibited by the additive.



The reverse of reaction I.24 will promote the radiolytic decomposition rather than protect it. The physical radiation protection process occurs favorably when the ionization and excitation potential of the additive are lower than the solvent molecules. Physical protection may also involve quenching and negative-ion formation (42).

(3) Kinetic Analysis

In a two component system where the components do not interact, it is assumed that the amount of radiolytic decomposition of a component is proportional to the amount of energy absorbed by that component. The amount of energy absorbed by a component is usually assumed to be proportional to its electron fraction in the system (43). This 'mixture law' is expressed mathematically in the following equation:

$$G(P) = G(P)_1 \epsilon_1 + G(P)_2 \epsilon_2 \text{ ----- I.26}$$

where the total G-value of product P is related to the electron fractions ϵ_1 and ϵ_2 of the components; $G(P)_1$ and $G(P)_2$ refer to the yields in the pure components. This equation is assumed to be valid in the present study, although Lamborn and Swallow (44) noted that this equation may not be justified if the two components have different excitation cross sections.

When the observed $G(P)$ deviates from the expected value, it is attributed to an interaction between the components. Both radical scavenging and physical protection mechanisms are responsible for a lower $G(P)$. The application of kinetic analysis to the cyclohexane-benzene system (41)

showed that charge transfer and/or energy transfer was the major effect at higher benzene concentration, but some other processes were significant at lower benzene concentration (electron fraction < 0.05).

(f) Deuterium Labelling and Isotope Effect

(1) Deuterium Labelling

It was mentioned that the scavengeable and unscavengeable processes can be differentiated by studying the effects of additives, whereas the various possible unscavengeable processes remain indistinguishable from one another. These unscavengeable processes may be further investigated through the radiolysis of partially and completely deuterated compounds, and a mixture of isotopic compounds. An analysis of the deuterium distribution in the final products will give valuable information on the different types of unscavengeable processes. An excellent example is illustrated in the radiolysis of ethylene. The radiolysis of C_2H_4 showed that hydrogen was a major product (45). The hydrogen yield remained unchanged when ethylene was irradiated with 5% of nitric oxide (46). This indicated that hydrogen formation was an unscavengeable process. When a mixture of C_2H_4 - C_2D_4 was irradiated, the hydrogen formed was mostly H_2 and D_2 (47)(48). This showed that hydrogen was formed by the unimolecular decomposition of ethylene. Since H_2 , HD , and D_2 were products in the radiolysis of both $CHDCHD$ and CH_2CD_2 , it was concluded that the two hydrogen atoms of a hydrogen molecule could be split from one carbon atom or two carbon atoms of the same molecule.

This kind of study also aids in elucidating the reactivity of the different bonds in a molecule. The radiolysis of deuterated ethanols has been investigated by Burr (49) and Myron (50). The values of the

deuterium contents in the total hydrogen yields are listed in Table I.1. The magnitudes of the contributions of the various groups in ethanol to the hydrogen forming reactions are in the following order:

methylene > hydroxyl > methyl

(2) Isotope Effect

The radiation kinetics of deuterium labelled organic compounds is always complicated by isotope effects (51)(52). Isotope effects are classified as primary or secondary, depending on whether or not the deuterium is involved directly in a bond cleavage or bond formation of a reaction.

A primary isotope effect is caused mostly by the lower zero point energy in the C-D bond compared to the C-H bond. The C-D bond dissociation energy is consequently higher by $\sim 1.2 \text{ kcal mole}^{-1}$ (52). An activation energy is required in the transformation of the reactants to the transition state that leads to the products. If the bond cleavage is complete in the transition state, the C-D will require a higher activation energy than the C-H bond. If a bond rupture is not involved in the transition state, then the isotope effect occurs when the carbon-hydrogen bond is tightened in the transition state. Quantum mechanical tunnelling (53)(54) (55), which is less probable for deuterium than for protium, may also contribute appreciably to the primary isotope effect.

The deuterium substitution at a certain part of a molecule can affect another part of the molecule only if there is a path of communication between the two parts. Hence, secondary isotope effects will probably be significant with molecules having π -bonds. In aliphatic compounds,

TABLE I.1

The Percentage of Deuterium in the Radiolytic Hydrogen from Liquid Ethanols

<u>% Deuterium in Hydrogen Yield</u>		
<u>Ethanol</u>	<u>Myron's Data (50)</u>	<u>Burr's Data (49)</u>
$\text{CH}_3\text{CH}_2\text{OD}$	35.0	34.2
$\text{CH}_3\text{CD}_2\text{OH}$	40.8	42.0
$\text{CD}_3\text{CH}_2\text{OH}$	6.9	4.2
$\text{CD}_3\text{CD}_2\text{OD}$	97.0	93-95

which have only σ -bonds, secondary isotope effects will probably be small. However, this effect can still be conveyed through inductive and hyperconjugative effects (52)(54)(56).

The most easily measurable isotope effect is called the overall isotope effect. It is defined as the yield of H_2 in the non-deuterated compound relative to the yield of D_2 in the perdeuterated counterpart, i.e. the ratio $G(H_2)/G(D_2)$. The overall isotope effects for the radiolysis of some compounds are listed in Table I.2. It is seen that these values range from 1 to 3. Theoretical calculations (51) show that the magnitude of an isotope effect varies with temperature and, at room temperature, it can attain a maximum value of 18 for C-H bonds. The competitive abstraction by methyl radicals from partially deuterated ethyl benzene has been investigated (57). *t*-Butyl peroxide, acetyl peroxide and photolysis of azomethane were employed as sources of methyl radicals. It was observed that the isotope effect (CH_4/CH_3D) changed from 19 at 50°C to 11 at 143°C.



Another criterion of isotope effects is the ratio γ/π (58), where γ and π are defined as

$$\gamma = \text{specific hydrogen yield} = \frac{G(H) \text{ per C-H bond in deuterated molecule}}{G(H) \text{ per C-H bond in non-deuterated molecule}}$$

$$\pi = \text{specific deuterium yield} = \frac{G(D) \text{ per C-D bond in deuterated molecule}}{G(H) \text{ per C-H bond in non-deuterated molecule}}$$

TABLE 1.2Overall Isotope Effect in the Radiolysis of Deuterated Compounds

<u>Compound</u>	<u>T°C</u>	<u>G(H₂)/G(D₂)</u>	<u>Phase</u>	<u>Reference</u>
C ₂ H ₄	25	1.0-1.54	gas	(59)(60)
C ₂ D ₄				
C ₂ H ₆	25	1.5	gas	(61)(62)
C ₂ D ₆				
C ₆ H ₆	25	3.0	liquid	(63)
C ₆ D ₆				
C ₂ H ₅ OH	25	1.28	liquid	(64)
C ₂ D ₅ OD				
C ₆ H ₁₀	25	1.98	liquid	(65)
C ₆ D ₁₀				
H ₂ O	20.5	0.95	liquid	(66)
D ₂ O				

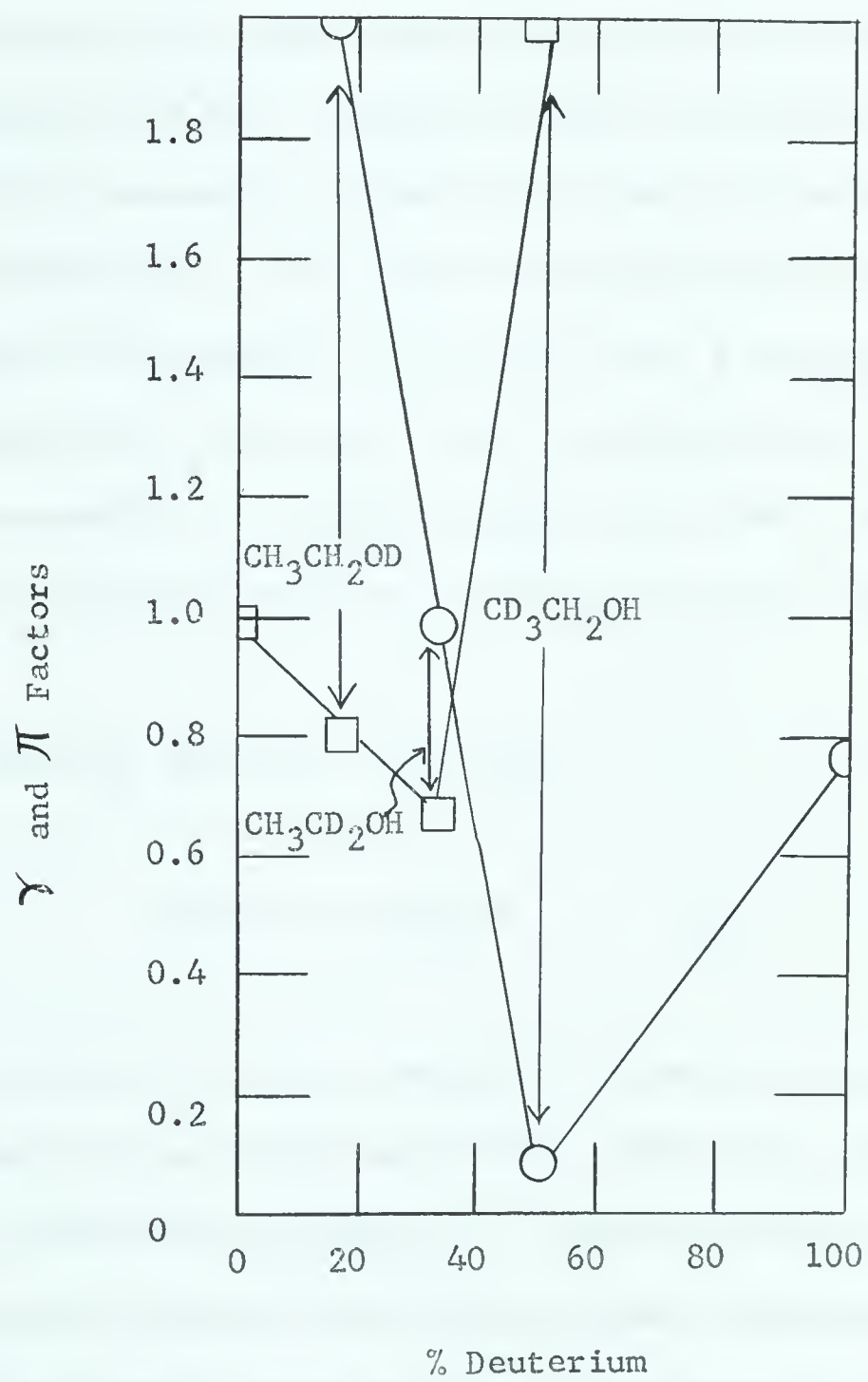
It is obvious that the ratio γ/π is the apparent isotope effect between a nondeuterated compound and its partially deuterated counterpart. The plot of γ and π factors as a function of deuterium content in the molecule will show clearly the selectivity of bonds. This has been done by Burr (58) for the radiolysis of ethanol. The data are reproduced in Figure I.1. The non-linearity of the curves shows that the C-H and O-H bonds are highly selective.

FIGURE I.1

The γ and π Factors in the Radiolysis of Ethanol

□ γ Factor

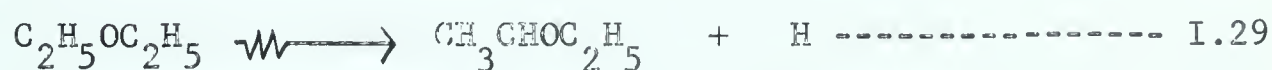
○ π Factor



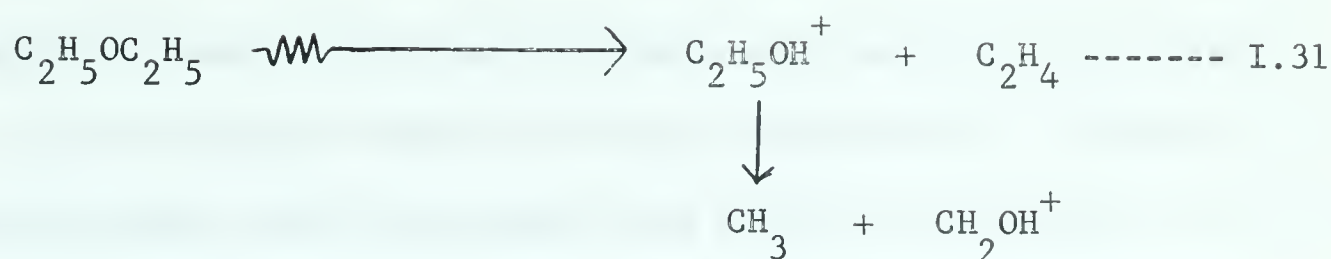
(B) PREVIOUS STUDIES OF THE RADIOLYSIS OF ETHERS

A survey of the liquid phase radiolysis of aliphatic ethers with helium ions was made by Newton (67). It was found that C-O bond cleavage was much more extensive than C-C bond cleavage in all cases. This conclusion was also drawn by McLafferty (21) in his mass-spectrometric analysis of ether fragmentation.

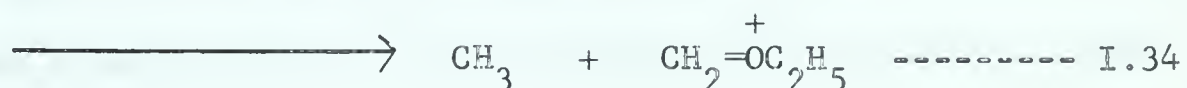
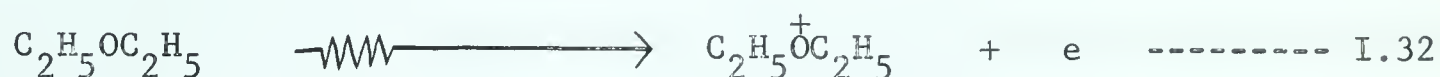
In the case of diethyl ether, Newton (67) found that the main products were hydrogen ($G=3.62$), ethylene ($G=1.07$), and ethane ($G=0.62$). The yields of carbonyl compounds, polymers, etc, were not determined because of experimental difficulties. The yields of hydrogen ($G=3.43$) and methane ($G=0.31$) were reported by Sedgwick et al (68) in the γ -radiolysis of ethyl ether. Using benzoquinone as an inhibitor, he concluded that 1.32 G unit of hydrogen is scavengeable. In spite of the lack of data, enough clues were obtained which suggested that the following reactions occur:



Reaction I.29 was supported by the paramagnetic resonance study of the γ -radiolysis of ethyl ether in the solid phase (69), which showed the probable existence of the radical $\text{CH}_3\text{CHOC}_2\text{H}_5$. Reaction I.30 was indicated by the abundance of ions of masses 28 and 31 in the mass spectrogram of ether (21)(70). They are probably formed by the rearrangement of a β -hydrogen atom, followed by the fission of the C-C bond:



The ion of mass 31 was shown to have a structure of CH_2OH^+ instead of CH_3O^+ (70). It is not yet known whether excited molecules or/and ionic species are involved. When a positive ion of ether is formed, the positive charge is usually located on the oxygen atom because the 2p electrons on O have the lowest ionization potential (71)(72)(73). The positive ion can dissociate by the removal of an α -H or a methyl group according to reaction I.33 and I.34 respectively:



The stabilization energy of a trivalent ion $=\text{C}=\text{O}^+$ was estimated to be 54 kcal mole⁻¹ (70).

Newton investigated the radiolysis of isopropyl ether (74) in more detail. A significant change in product distribution was observed when ether was irradiated with helium ions, electrons, and γ -rays. Newton concluded that "the primary radicals escape from the spurs more effectively with γ -ray irradiations than in helium ions or electron irradiations, hence, yield products by radical-molecule reactions (hydrogen abstractions) rather than radical-radical processes". The increase of temperature also affects the product distributions owing to "a more rapid diffusion of the radicals

from the tracks and spurs, resulting in less recombination of the primary radicals to reform isopropyl ether at the high temperature". Additive studies were also made using acetaldehyde and iodine as inhibitors. As a result of these observations, the following possible mechanisms were postulated:



The excited molecule and the six radicals, with varying amounts of energy will react in the spur or in the bulk resulting in the formation of products.

Newton's results were in good agreement with the work of Bach (75), and Saraeva et al (76).

(C) THE SCOPE OF THE PRESENT INVESTIGATION

The present investigation dealt mainly with the Co^{60} γ -radiation induced decomposition of diethyl ether in the liquid phase. All the observed products were studied as function of dose and concentration of additives. Some experiments were done in the gas phase for the purpose of comparison.

The mechanism for the radiolytic decomposition of ethyl ether will be compared with ethanol and water.

SECTION II - EXPERIMENTAL(A) MATERIALS(a) Compounds to be Radiolized(1) Ethyl Ethers

Diethyl ether, Spectro Grade, was obtained from Eastman Organic Chemicals Co. No impurities were found on gas chromatographic analysis using four different columns—silicone grease, ucon, di-2 ethyl hexyl sebacate, and tetraethylene glycol dimethyl ether. It was used as supplied. Radiolysis of ether that had been dried over sodium was also done. No differences in yields were observed.

Three deuterated ethers — d_{10} , α - d_4 , β - d_6 , were obtained from Merck, Sharp & Dohme of Canada Limited. They were used as supplied. The impurities are given in Table II.1.

(2) Ethyl Vinyl Ether

Ethyl Vinyl Ether (Eastman Organic Chemicals Co.) was purified with .g.c.^a using a column of tetraethylene glycol dimethyl ether on Chromosorb W. The process reduced the impurities to less than 1.0%.

(3) Benzene

Research grade benzene from Phillips Petroleum Co. was used as supplied.

(4) 1,3-Pentadiene

1,3-Pentadiene from Columbia Organic Chemicals Co., Inc.

a: g.c. refers to gas chromatography

TABLE II.1Impurities in the Deuterated Ethers

	<u>Impurities</u>	<u>%</u>
1. <u>$(\text{CH}_3\text{CD}_2)_2\text{O}$</u>		
	α -H/ α -D	4.2
	β -D/ β -H	4.3
	Acetone	0.7
	A ^a	0.05
	B	0.08
	C	0.5
	D	1.3

2. <u>$(\text{CD}_3\text{CD}_2)_2\text{O}$</u>		
	α -H/ α -D	9
	β -H/ β -D	0.6
	Acetone	0.4
	Methyl ether	0.2

3. <u>$(\text{CD}_3\text{CH}_2)_2\text{O}$</u>		
	α -D/ α -H	25
	β -H/ β -D	18
	E	0.1
	F	0.1
	G	0.2

a: A, B, C... refer to unidentified impurities.

was used as supplied.

(5) Acetone

Acetone from Mallinckrodt Chemical Works Ltd. was used as supplied.

(b) The Compounds used for Identification and Calibration Standards

The compounds used are listed on Table II.2.

TABLE II.2

<u>No.</u>	<u>Compound</u>	<u>Supplier</u>
1.	Acetal	Eastman Organic Chemicals Co.
2.	Acetaldehyde	The British Drug Houses Ltd.
3.	Acetylene	Matheson of Canada Ltd.
4.	n-Butane	Phillips (Research Grade)
5.	s-Butyl Ethyl Ether	Delta Chemical Works, Inc.
6.	n-Butyl Ethyl Ether	K & K Laboratories, Inc.
7.	Carbon Monoxide	Matheson of Canada Ltd.
8.	2,3-Diethoxybutane	Home-made
9.	1,2-Diethoxyethane	Eastern Chemicals
10.	Diethoxymethane	Eastman Organic Chemicals Co.
11.	1,2-Diethoxypropane	Delta Chemical Works, Inc.
12.	Ethane	Phillips (Research Grade)
13.	Ethanol (Anhydrous)	Reliance Chemical Ltd.
14.	Ethylene	Phillips (Research Grade)
15.	Ethyl Methyl Ether	Frinton Lab.
16.	Ethyl i-Propyl Ether	K & K Laboratories, Inc.

TABLE II.2 (Cont'd)

<u>No.</u>	<u>Compound</u>	<u>Supplier</u>
17.	Ethyl n-Propyl Ether	Delta Chemical Works, Inc.
18.	Ethyl Vinyl Ether	Eastman Organic Chemicals Co.
19.	Formaldehyde Solution	Fischer Scientific Company
20.	Hydrogen	Canadian Liquid Air Company Ltd.
21.	Hydrogen-d ₁	Home-made
22.	Hydrogen-d ₂	Matheson of Canada Ltd.
23.	Methane	Merck & Co. Limited
24.	Methane-d ₁	" " "
25.	Methane-d ₂	" " "
26.	Methane-d ₃	" " "
27.	Methane-d ₄	" " "

1, 9, and 10 were distilled before used.

8 was prepared using Moore's method (77). Di-tert-butyl peroxide (pract.), supplied by Matheson, Coleman & Bell, was mixed with ethyl ether in a one to three mole ratio. The mixture was allowed to react for two days in a sealed capsule at 145°C. The product was purified by g.c.^a using a silicone grease column. It contained 3% impurities.

14, 15 were purified by g.c., using respectively, a tetraethylene glycol dimethyl ether and a ucon column. 16 was purified as in (a). 14, 15, and 16 had less than 1.0% impurities after purification.

21 was made by subjecting an equimolar mixture of hydrogen and deuterium to electric discharge.

All other compounds were used as supplied.

a: g.c. refers to gas chromatography

(c) Compounds used for Gas Chromatographic AnalysisTABLE II.3

<u>No.</u>	<u>Compound</u>	<u>Supplier</u>
1.	Celite(Komat Ce) ^r	Burrell Corp.
2.	Charcoal	" " (High Activity)
3.	Di-2 Ethyl Hexyl Sebacate on Chromosorb W	Matheson of Canada Ltd.
4.	Helium	Air Reduction Canada, Ltd.
5.	Silica Gel	Burrell Corp. (Medium Activity)
6.	Silicone Grease	Dow Corning
7.	Tetraethylene Glycol Dimethyl Ether on Chromosorb W	F& M Scientific Corp.
8.	Ucon LB 1800X	Carbide & Carbon Chemicals Co. Ltd.

(B) APPARATUS(a) High Vacuum System

A high vacuum system was necessary for sample preparation and gas analysis. It was a structure of Pyrex glass tubing, stopcocks, and traps (Figure II.1). Stopcocks S_1 , S_2 and joints J_1 , J_2 were greased with Apezion N, manufactured by Associated Electric Industries Ltd. Silicone grease (Dow Corning) was used for the rest. The system was evacuated with a mercury diffusion pump and a Welch duo-seal rotary vacuum pump (W.M. Welch Manufacturing Co.; Model 1405-6). The Pirani gauge (Type CE 120) was manufactured by Continental Electric Co. It was calibrated against a Mcleod gauge before use. In operation, the trap T_1 was partly submerged in liquid nitrogen. It trapped off condensable vapors. When the system was not in operation, the liquid nitrogen was removed from trap T_1 and stopcock S_3 was opened to the atmosphere. Trap T_2 collected mercury that distilled out of the diffusion pump. The main manifold was slightly inclined so that mercury that got into it accidentally would collect in the finger F_1 and could be removed. All stopcocks, S_4 - S_9 , were connected to the upper surface of the manifold so that mercury could not collect in them.

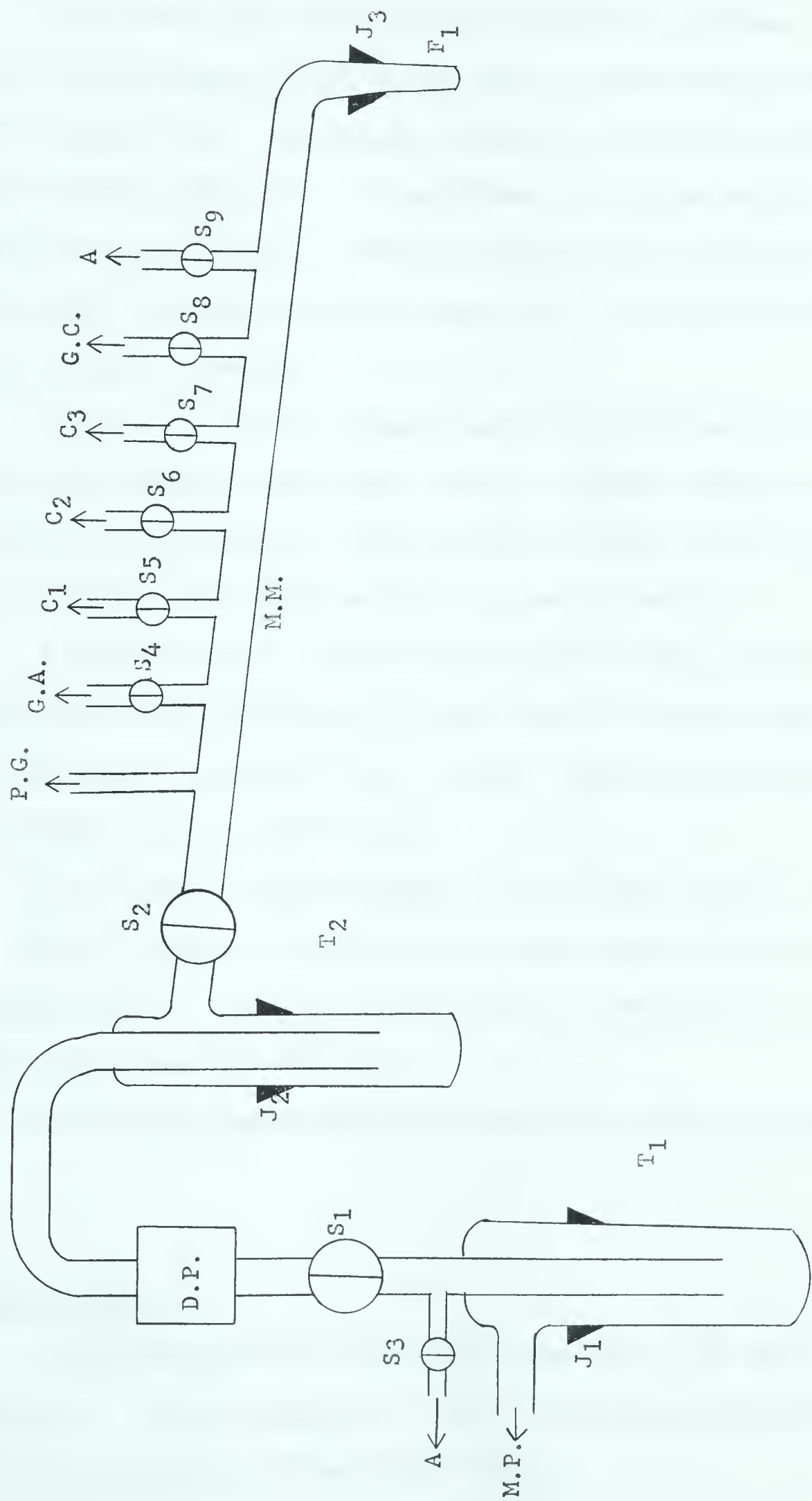
Stopcock S_4 connected the main manifold to the gas analysis system (Page 40). Stopcocks S_5 , S_6 , and S_7 connected the main manifold to the substrate system (Page 36), the inhibitor system (Page 36), and the sampling system (Page 36), respectively. Stopcock S_8 led to the gas calibration system (Page 43). Stopcock S_9 was a vent for glass blowing.

(b) The Gas Chromatography System

The system is shown schematically in Figure II.2. Copper tubing is designated by a solid line and electric wire by a dotted

FIGURE II.1High Vacuum System

A	Atmosphere
C ₁	Substrate System
C ₂	Sampling system
C ₃	Inhibition system
D.P.	Mercury diffusion pump
F ₁	Finger
G.A.	Gas analysis system
G.C.	Gas calibration system
J ₁ and J ₂	45/50 joints
J ₃	12/30 joints
M.M.	Main manifold
M.P.	Welch mechanical vacuum pump
P.G.	Pirani gauge
S ₁ and S ₂	10 mm bore stopcocks
S ₃ to S ₉	4 mm bore stopcocks
T ₁ and T ₂	Traps



line.

The carrier gas, helium passed through the reference of the detector cell (Gow-Mac Model TR II B), the g.c. column and the sampler side of the detector cell. Helium was adjusted to a pressure of 20 lb/sq. in. by a pressure gauge P.G. It was dried in a drying tube D.T. filled with molecular sieve (No. 13X). Carrier flow-rate was controlled by the fine control valve F.A. (Edwards High Vacuum Ltd.). The flow-rate was measured by a bubble flowmeter.

The g.c. columns, wrapped evenly with nichrome heating wire, were heated to the required temperature using a variable voltage power supply. The temperature was read off the dial thermometer (Fisher Scientific Co.). A list of the columns and conditions used is given in Table II. 4.

D.G. was a device used for the analysis of gas products (Page 38). When liquid products were analysed, D.G. was removed, and the rubber tubing R.T.₁ was connected to the inlet H.I.₂. Liquid samples were injected by a hypodermic syringe at the inlet H.I.₁.

The recorder was manufactured by E.H. Sargent and Co. (Cat. No. S-72180). It was connected in series to the power supply (Model 9999-c) and the detector cell. The detector was kept at a temperature of 400°F. The detector current used was 200 ma.

The attached gas calibration system G.C. will be described on Page 43.

(c) Miscellaneous

A Metropolitan-Vicker MS 2 mass spectrometer was used in gas product analysis. It was especially useful in the analysis of isotopic hydrogen from the radiolysis of deuterated ethers.

FIGURE II.2The Gas Chromatography System

B	500 ml bulb
B.F.	Bubble flowmeter
C.C.	Burrell type heated V.P.C. column
D	Drying tube
D.C.	Hot wire detector cell
D.G.	Device for analysis of gas products
D.T.	Dial thermometer
F.A.	Fine flow control valve
G.C.	Gas calibration system
G.I.	Gas Inlet
G.S.	Gas Sampler
He	Helium supply
H.I. ₁ and H.I. ₂	Helium inlets
M	Manometer
M.M.	Main vacuum manifold
P	Metal plunger
P.G.	Pressure gauge
P.S.	Gow-Mac power supply
R	Recorder
R.T. ₁ , R.T. ₂ , and R.T. ₃	Rubber tubings
S ₁ to S ₄	Stopcocks
S.B.	Sample bulb of ether
T	Trap
V	Variable voltage power supply

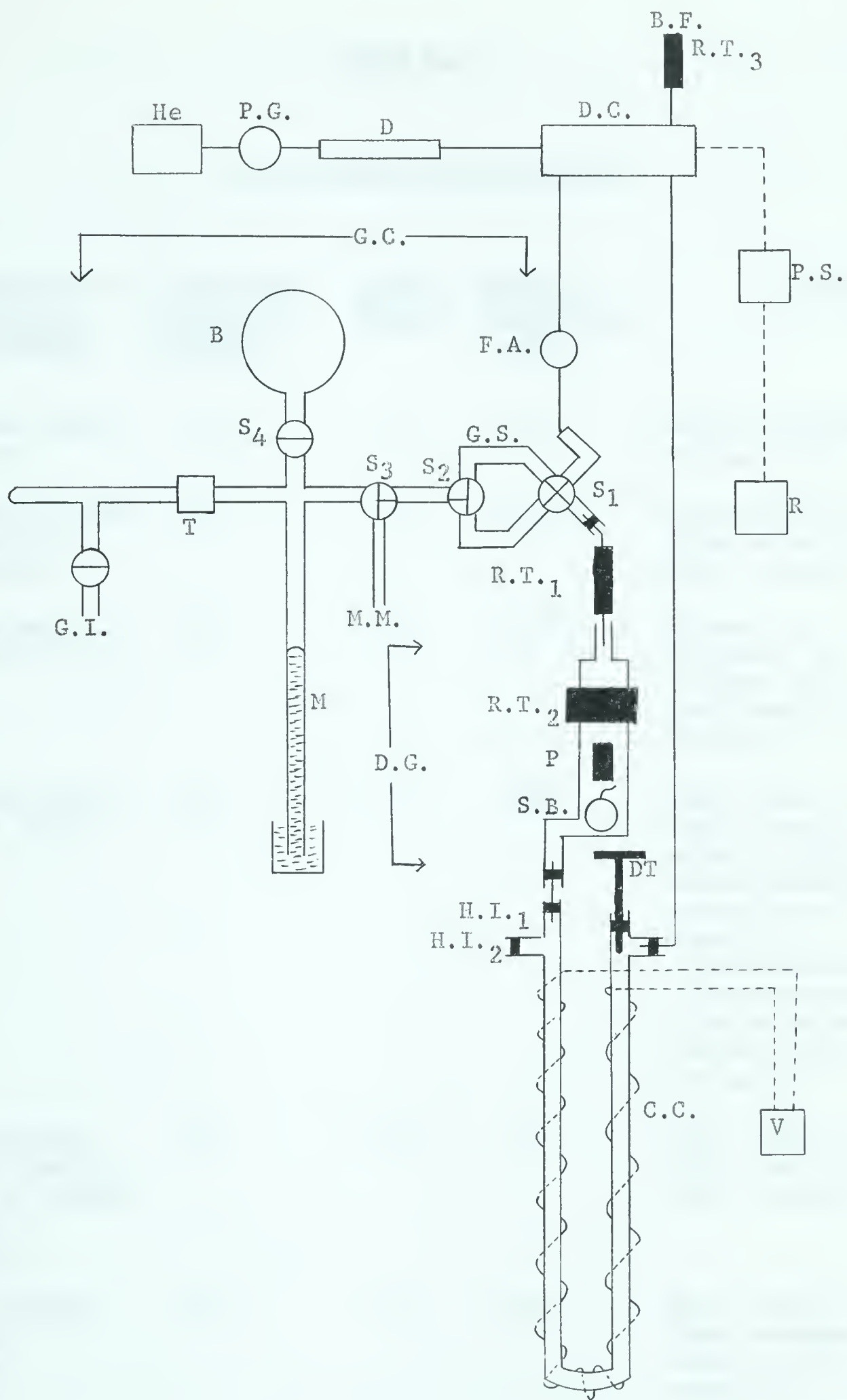


TABLE II.4

G.C. Columns and Conditions

<u>Column packing, composition (% by weight)</u>	<u>Carrier gas flow rate (ml/min)</u>	<u>Length (Meter)</u>	<u>Maximum Temperature (°C)</u>	<u>Voltage</u>
1. Charcoal, high activity	80	1.0	25	Carbon monoxide, 1½; Methane, 4½
2. Di-2 ethyl hexyl sebacate on chromosorb W	150	2.5	25-100	Acetaldehyde, 2; Ethyl ether, 6; Ethyl i-propyl ether, 8
3. Silica gel, medium activity	100	2.5	25-100	Ethane, 2; Ethylene, 2½; Propane, 3½; Acetylene, 4½; Butane, 6½
4. Silicone grease 25% on Celite	167	2.5	190	Ethyl ether, 2; Ethyl i-propyl ether, 4; s-Butyl ethyl ether, 7; Diethoxymethane, 8; n-Butyl ethyl ether, 8½ ; Acetal, 10; 1,2-Diethoxyethane, 12; 1,3-Diethoxypropane, 12½; 2,3-Diethoxybutane, 13½ ; Unknown ₁ , 14½; Unknown ₂ , 16
5. Tetraethylene glycol dimethyl ether on chromosorb W + column 6	214	4.0	25	Ethyl ether, 6; Ethyl vinyl ether, 9½; Ethyl i-propyl ether 10½
6. Ucon LB1800X 25% on celite	230	1.5	0-155	Ethyl ether, 2; Ethyl n-propyl ether, 4; s-Butyl ethyl ether, 5½; Ethanol, 6; 2,3-Diethoxybutane, 9½

An N.M.R. spectrometer (Varian HR 100), operated at 100 MC, was used for the detection of isotopic impurities in the deuterated ethers.

A Cary spectrophotometer (Model 14) was used for the analysis of ferric ion concentration in Fricke dosimetry (Page 38).

(C) PROCEDURE(a) Sample Preparation

The apparatus for sample preparation is shown in Figure II.3. It consisted of a substrate system Su.S. on the left, the inhibitor system I.S. on the right, and the sampling system Sa.S. in the middle. The substrate, ethyl ether, was introduced into the substrate system from finger F_1 . It was degassed, transferred, in vapor form, into the measuring system. The volume of the measuring system was calibrated. The manometer was used to measure the pressure with the aid of a cathetometer (Griffin & George Ltd.). The amount of ethyl ether in the calibrated volume was calculated by the simple gas law equation. The ether was finally condensed in a sample tube or bulb and sealed off with a flame.

For liquid phase radiolysis, sample tubes of the type S.T.₁ and S.T.₂ were used for the analysis of hydrogen and liquid products. The small bulb S.B.₁ was used for the analysis of all gas products except hydrogen.

For gas phase radiolysis, the S.B.₂ type of sample bulb was used. It was a 500 ml bulb with a breakseal attached.

The inhibitor system was similar to the substrate system. The only difference was that a 500 ml bulb was used instead of a 2 litre bulb. Benzene, ethyl vinyl ether and 1,3 pentadiene were used as inhibitors.

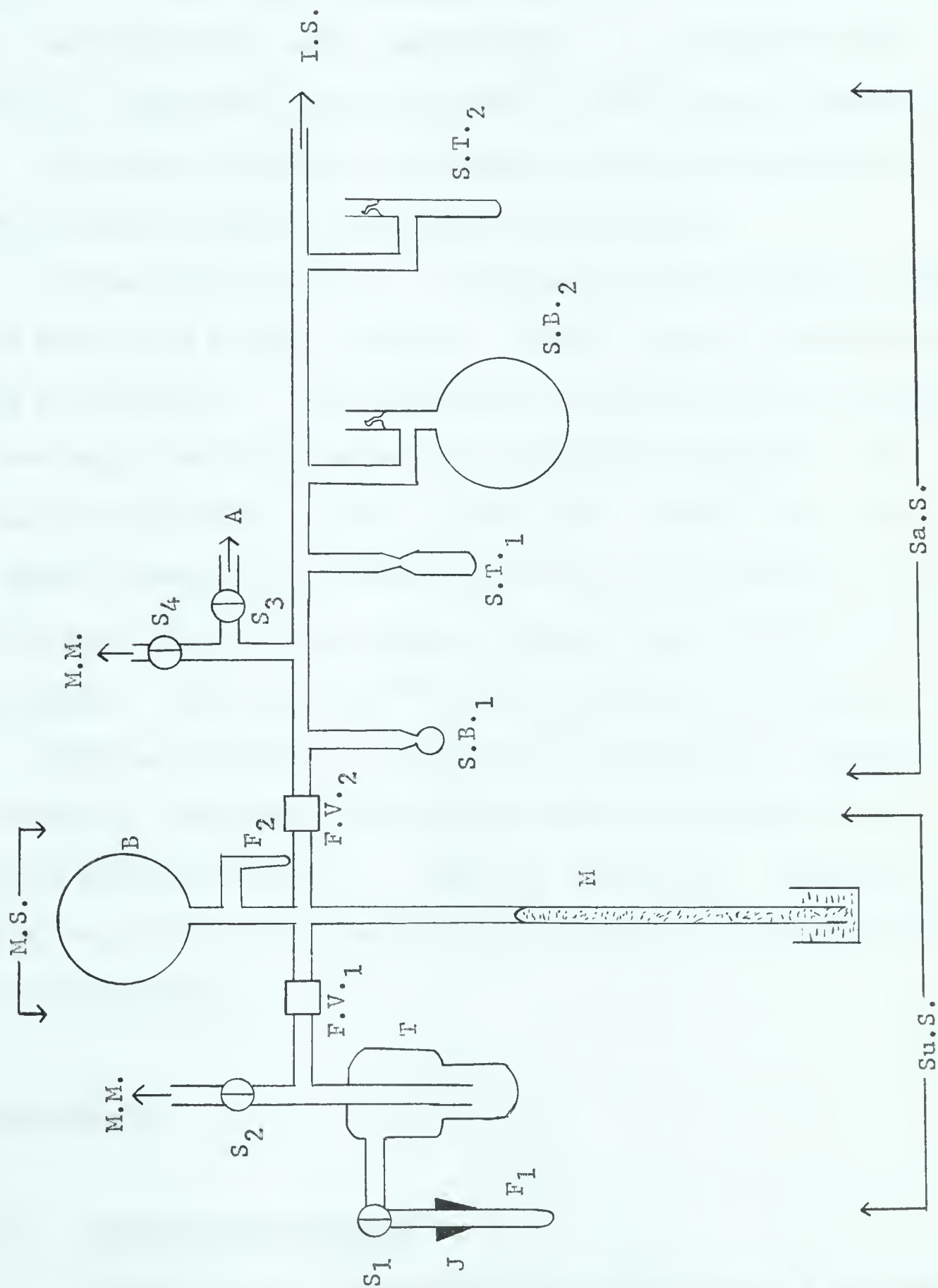
Since the amounts of both substrate and inhibitor were known, the percentage of the latter could be calculated.

(b) Sample Irradiation

The samples were irradiated at assigned positions near the

FIGURE II.3Apparatus for Sample Preparation

A	Atmosphere
B	2 litre bulb
F ₁ and F ₂	Fingers
F.V. ₁ and F.V. ₂	Mercury float valves
I.S.	Inhibitor system
J	12/30 joint
M	Manometer
M.M.	Main vacuum manifold
M.S.	Measuring system
S ₁ , S ₂ , S ₃ and S ₄	4 mm stopcocks
Sa.S.	Sampling system
S.B. ₁	Small sample bulb, Diameter 11-12mm
S.B. ₂	500 ml sample bulb
S.T. ₁ and S.T. ₂	Sample tubes, outside diameter 15 mm
Su.S.	Substrate system
T	Trap



radiation source. The dose-rates of the assigned positions were obtained by chemical dosimetry.

Two Co^{60} γ -ray sources were used. One of them was a 300 curie source. The dose-rates used ranged from 4×10^{18} to 8×10^{18} ev/gm of ether-hr. The other source was a Gammacell 220. It contained 12,300 curies of Co^{60} . Dose-rates used were 5×10^{19} - 7×10^{19} ev/gm of ether-hr.

Two kinds of dosimetry were used for dose-rate determination — Fricke for liquid samples and ethylene for gas samples.

Fricke dosimetry (78): a solution of $0.001 \text{ M Fe}(\text{NH}_4)\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and 0.001 M NaCl in $0.8 \text{ N H}_2\text{SO}_4$ was used. Ferrous ions were converted into ferric ions by radiolysis. The concentration of ferric ions was measured by a Cary recording spectrophotometer at a wavelength of $304 \text{ m}\mu$. The molar extinction coefficient was 2201 at 25°C (78). $G(\text{Fe}^{+3})$ was 15.6. Since the energy absorbed was proportional to the electron density of the material, the dose-rate for ether samples or other samples could be calculated accordingly. The decay of Co^{60} was also taken into consideration.

Ethylene dosimetry: a 500ml bulb of ethylene at a pressure of about 740 mm was irradiated. The hydrogen yield was measured by the Toepler-McLeod apparatus (Page 40). $G(\text{H}_2)$ was 1.28 (79). The trap T_2 (Figure II.4) was filled with molecular sieve to prevent the ethylene from entering the McLeod gauge.

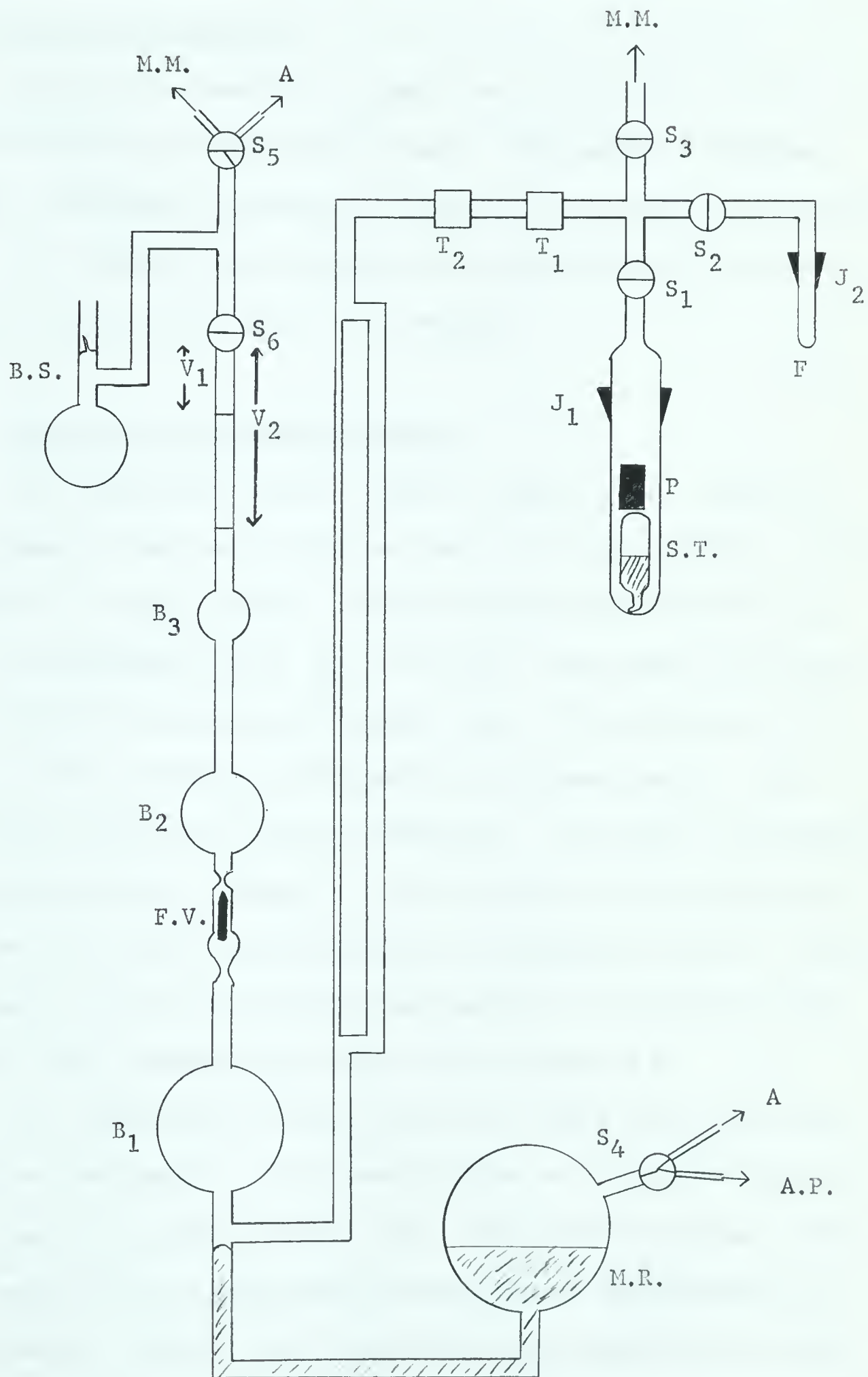
(c) Gas Analysis

(1) Light Ether Radiolysis

CO and C_1 to C_2 hydrocarbons were analyzed by g.c. using a special device, D.G. (Figure II.2). An irradiated sample bulb S.B.₁

FIGURE II.4Gas Analysis & Toepler Mcleod System

A	Atmosphere
A.P.	Auxiliary pump
B ₁ - B ₃	500,50, and 10 ml bulbs
B.S.	Breakseals
F	Finger
F.V.	Float valve
J ₁	24/40 joint
J ₂	12/30 joint
M.M.	Main vacuum manifold
M.R.	1 litre mercury reservoir
P	Metal plunger
S ₁ and S ₆	4 mm stopcocks
S.T.	Sample tube
T ₁ and T ₂	Traps
V ₁ and V ₂	Calibrated volumes



(Figure II.2) was broken inside D.G. by a plunger P. The whole sample was carried by helium to a particular g.c. column. The columns used were calibrated, as discussed on page 43.

Hydrogen was measured, together with CO and CH₄, as the -196°C fraction in the Mcleod gauge (see below). The amount of hydrogen was obtained by subtracting the amount of CO and CH₄ from the total fraction.

Some samples were analyzed by mass spectrometer (see below). The results were identical with the g.c. analysis.

(2) Radiolysis of Deuterated Ethers

The analytical system is shown in Figure II.4. Traps T₁ and T₂ and the sample itself were cooled by dewars of liquid nitrogen. The sample was broken by a metal plunger. Ether distilled gradually into T₁ and T₂. The non-condensable gases, H₂, CO and CH₄, were pumped continually into the Mcleod gauge by operating the Toepler pump. The pumping was continued until a constant reading was obtained on the Mcleod gauge. This fraction was transferred to B.S. and was sealed off. The ether collected in T₁ and T₂ was distilled into a finger F. The distillation and pumping process was repeated twice with T₁ and T₂ cooled by isopentane slush (~ -155°C). All C₂'s and some C₃'s were now collected and measured in the Mcleod gauge. This fraction was then condensed and sealed off in another B.S.

The compositions of both fractions (-196°C and -155°C) were analyzed by a mass spectrometer. The sensitivities of all gas products on the mass spectrometer are given on Table II.5. The -155°C fraction of deuterated ether samples was too complicated to be analyzed quantitatively on the mass spectrometer. However, the relative isotopic composition of ethylene and ethane could be determined. This was done by analyzing the samples

TABLE II.5Gas Sensitivities for the Mass Spectrometric Analysis

<u>Compound</u>	<u>m/e</u>	<u>Sensitivity</u> (<u>cm/micron</u>)
Carbon monoxide	28	2.130
Ethane	30	0.484
Ethane	27	0.640
Ethane	26	0.460
Ethylene	27	0.854
Ethylene	26	0.830
Hydrogen	2	0.616
Hydrogen-d ₁	3	0.701
Hydrogen-d ₂	4	0.753
Methane	16	1.140
Methane-d ₁	16	0.935
Methane-d ₁	17	1.140
Methane-d ₂	18	1.150
Methane-d ₂	17	0.775
Methane-d ₂	16	0.375
Methane-d ₃	19	1.140
Methane-d ₃	18	0.541
Methane-d ₃	17	0.624
Methane-d ₃	16	0.087
Methane-d ₄	20	1.140
Methane-d ₄	18	1.022

TABLE II.5 (cont'd)

<u>Compound</u>	<u>m/e</u>	<u>Sensitivity</u> (<u>cm/micron</u>)
Methane-d ₄	16	0.180
Propane	44	0.450
Propane	43	0.440
Propane	27	0.720
Propane	26	0.140

at low energy scans (10-12ev). The parent peaks of the ethylenes and ethanes were compared, assuming that the sensitivities were unaffected by deuteration.

(d) Liquid Analysis

An irradiated ether sample was broken open by a metal plunger inside a tube plugged with a neoprene seal. This kept the ether from evaporating. 0.08 ml to 0.1 ml of ether was extracted into a 0.1 ml hypodermic syringe through the seal. This was injected into the required g.c. column. The calibrations of various products will be described below.

The chromotropic method (80) was used for formaldehyde analysis.

(e) Calibration of Radiolytic Products on G.C. Columns

(1) Gases

A gas calibration system, G.C. in Figure II.2, was used for this purpose. The gas to be calibrated was introduced from a gas inlet G.I. into a storage bulb B. The gas was then introduced in various quantities into the gas sampler G.S. The volume of the gas sampler was calibrated. The pressure of the gas was measured by the manometer with the aid of a cathetometer. The known amount of gas was then used to calibrate the adjacent gas chromatography system.

(2) Liquid Products

Standard solutions of the compounds to be calibrated were prepared in ethyl ether for this purpose. Some of the calibration factors varied with concentration. Therefore, the concentrations of the solutions

were prepared as close as possible to those of the samples to be analyzed.

(f) Calibration Factors for G.C. Columns

(1) Gases

The calibration factors for gases were expressed as the number of molecules per unit gas chromatographic peak area. The calibration factors are plotted against pressure in Figure II.5. They were found to be independent of pressure. Therefore, the average calibration factor was used for each gas. The average calibration factors are given on Table II.6. The calibration factor for ethylene was also used for acetylene because of their similarity in carbon numbers and bond structure.

(2) Liquid Products

The calibration factors for liquid products were defined as the mole ratio divided by the area ratio, where

$$\text{mole ratio} = \frac{\text{Mole of Product}}{\text{Mole of Ether}}, \quad \text{and}$$

$$\text{area ratio} = \frac{\text{Area of Product}}{\text{Area of Ether}}$$







The variation of calibration factors with area ratio is given on Table II.7. Graphical representations of these data are given in Figure II.6 to Figure II.9 inclusive.

(g) Gas Sensitivities on Mass Spectrometer

The sensitivities, in cm/micron of all gas products are given on

Table II.5. Since the sensitivities changed from day to day, new measurements were made for each series of analysis.

FIGURE II.5Calibration Factors

	Butane
	Carbon Monoxide
	Ethane
	Ethylene
	Methane
	Propane

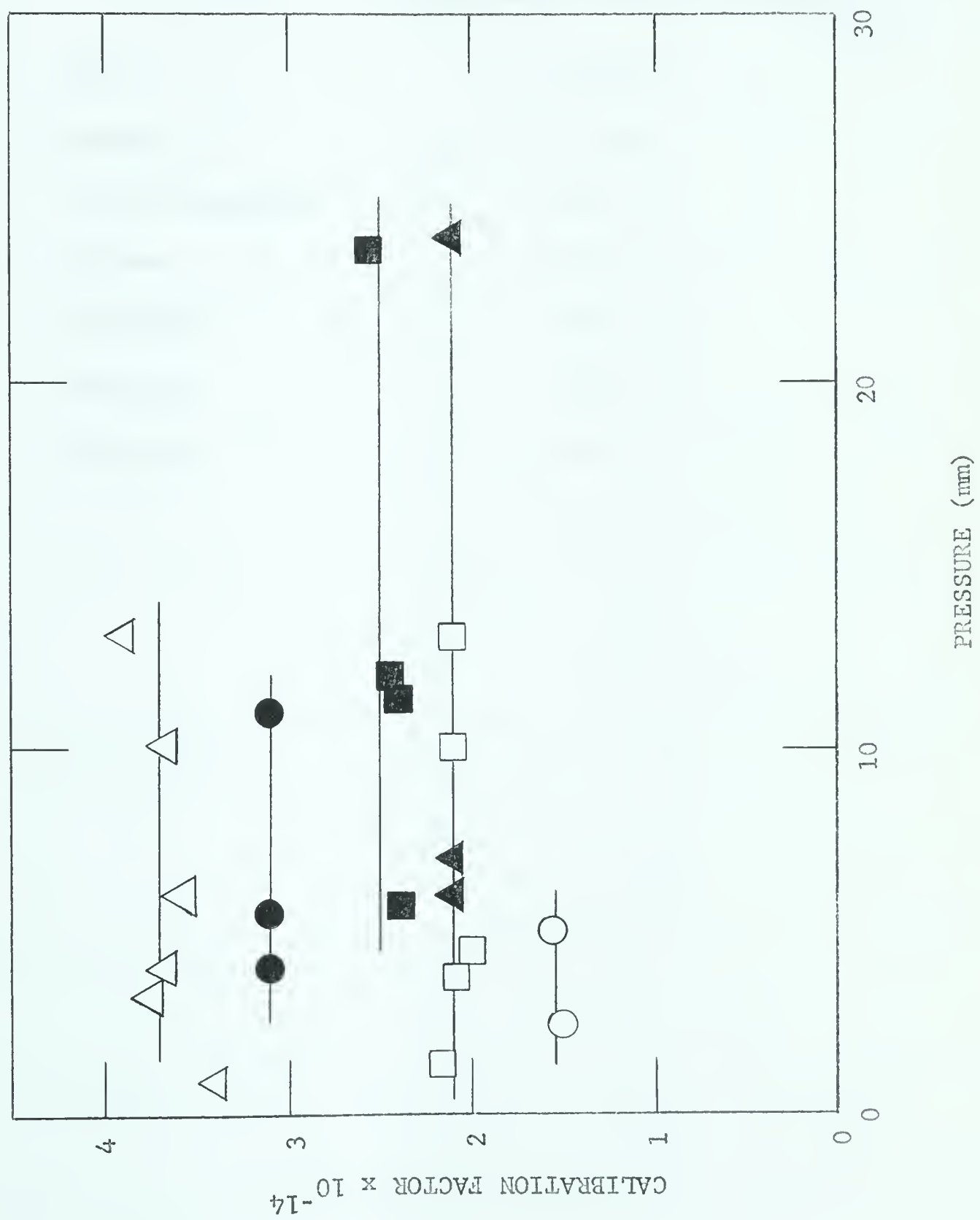


TABLE II.6Average Calibration Factors for Gas ProductsCalibration Factor (Average)

Gas	$\times 10^{-14}$
Butane	1.54
Carbon monoxide	3.1
Ethane	2.1
Ethylene	2.4
Methane	3.7
Propane	2.1

TABLE II.7

Calibration Factors for Liquid Products

<u>Compound calibrated</u>	<u>G.C. Column</u>	<u>Area Ratio x 10³</u>	<u>Factor</u>	<u>Graphical Representation (Figure)</u>
Acetal	Silicone grease on celite	0.136 0.280 1.160 6.160	1.2 1.5 1.6 1.5	II.6
n-Butyl ethyl ether	Silicone grease on celite	0.141 0.340 0.84 6.500	0.72 0.87 0.94 0.84	II.6
s-Butyl ethyl ether	Silicone grease on celite	0.278 0.567 1.273	1.3 1.3 1.3	II.7
s-Butyl ether ether	Ucon on celite	0.306 0.313 0.715 0.869 1.355	1.2 1.1 1.1 1.1 1.1	II.7
2,3-Diethoxy- butane	Silicone grease on celite	0.860 0.895 1.310 1.690 2.600 2.780	1.26 1.29 1.5 1.35 1.24 1.50	II.7
2,3-Diethoxy- butane	Ucon on celite	0.901 1.820 3.360	1.2 1.2 1.1	II.8
1,2-Diethoxy- ethane	Silicone grease on celite	0.910 2.800 4.100	0.95 0.92 0.95	II.8
Diethoxy- methane	Silicone grease on celite	0.111 0.256 0.832 7.040	1.0 1.1 1.1 1.0	II.9

TABLE II.7 (cont'd)

<u>Compound calibrated</u>	<u>G.C. Column</u>	<u>Area Ratio x 10³</u>	<u>Factor</u>	<u>Graphical Representation (Figure)</u>
1,2-Dieth- oxypropane	Silicone grease on celite	Use that of 2,3-diethoxybutane		
Ethanol	Ucon on celite	0.067	0.79	II.8
		0.140	0.77	
		0.260	0.80	
		0.291	0.78	
		0.800	0.85	
		1.900	0.79	
Ethyl i- propyl ether	Silicone grease on celite	0.122	1.2	II.9
		0.33	1.4	
		0.67	1.1	
Ethyl i- propyl ether	Di-2 ethyl hexyl sebacate	0.11	1.7	II.8
		0.53	1.2	
		2.04	0.94	
Ethyl n- propyl ether	Ucon on celite	0.80	1.4	II.9
		2.67	0.98	
		6.1	0.81	
Ethyl vinyl ether	Tetraethylene glycol dimethyl ether on chromosorb and ucon on celite	0.62	1.59	II.7
		1.2	1.37	
		2.46	1.1	
Unknown ₁	Silicone grease on celite	Use that of 2,3-diethoxybutane		
Unknown ₂	Silicone grease on celite	Use that of 2,3-diethoxybutane		
Acetaldehyde	Di-2 ethyl hexyl sebacate	0.76	0.99	II.9
		1.21	0.92	
		4.93	0.87	

FIGURE II.6Calibration FactorsA

Compound: n-Butyl ethyl ether

Column: Silicone grease

B

Compound: Acetal

Column: Silicone grease

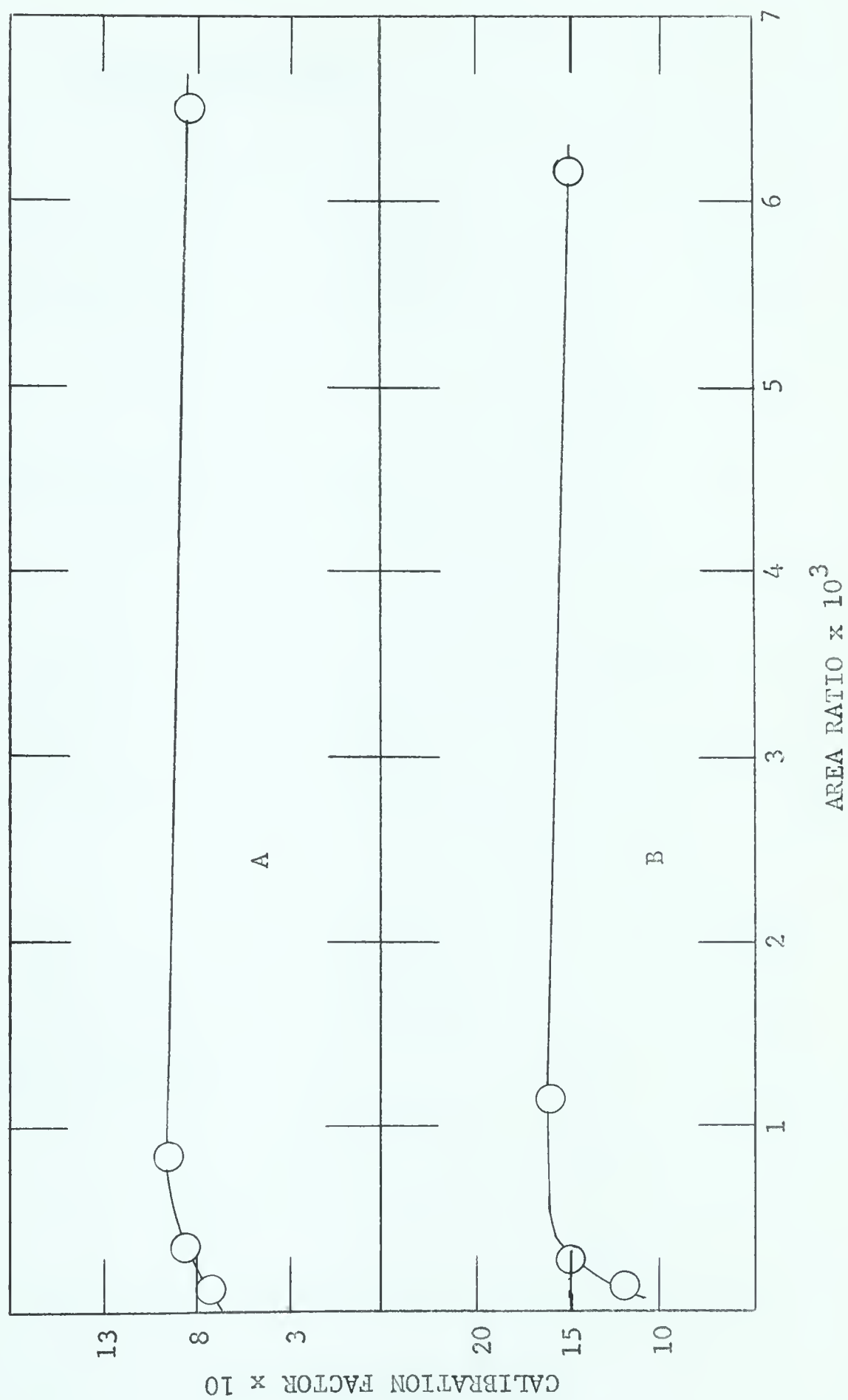


FIGURE II.7Calibration FactorsA

Compound: i-Butyl ethyl ether

Column: Silicone grease

B

Compound: i-Butyl ethyl ether

Column: Ucon

C

Compound: 2,3-Diethoxybutane

Column: Silicone grease

D

Compound: Ethyl vinyl ether

Column: Tetrethylene glycol dimethyl
ether on chromosorb w and
Ucon on celite

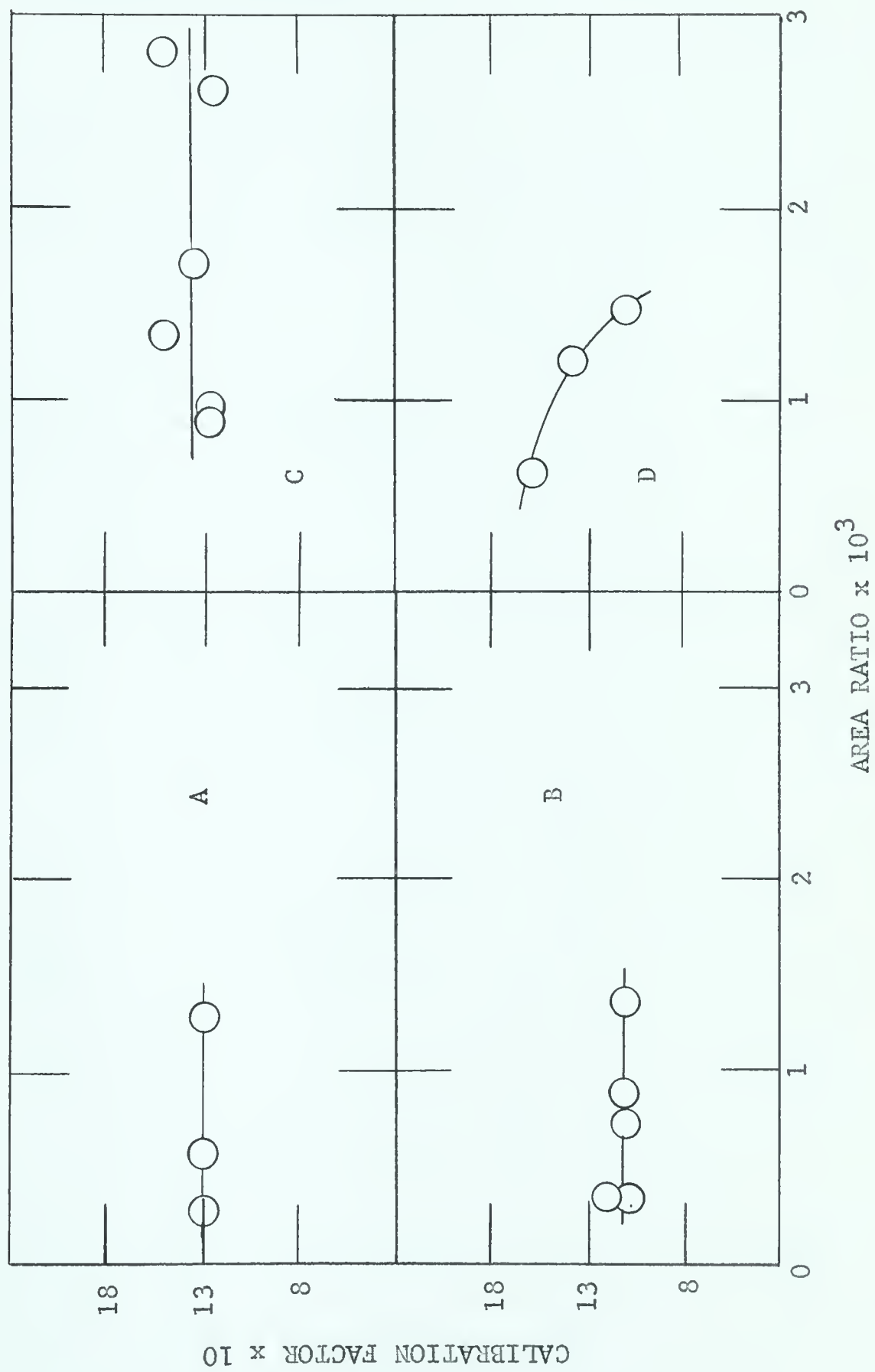


FIGURE II.8Calibration FactorsA

Compound : 2,3-Diethoxybutane

Column : Ucon

B

Compound : 1,2-Diethoxyethane

Column : Silicone grease

C

Compound : Ethanol

Column : Ucon

D

Compound : Ethyl i-propyl ether

Column : Di-2 ethyl hexyl sebacate

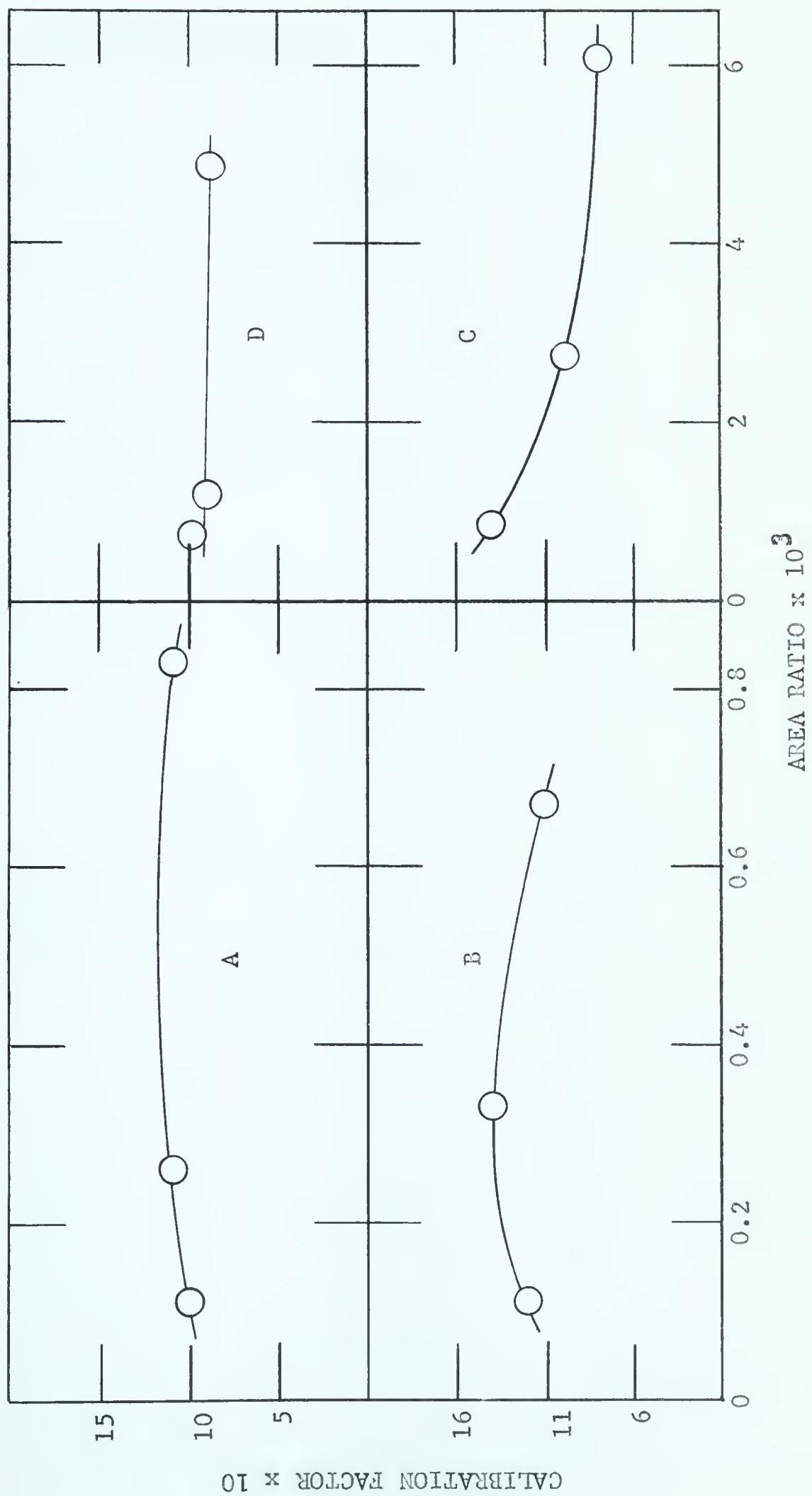


FIGURE II.9Calibration FactorsA

Compound: Diethoxymethane
Column: Silicone grease

B

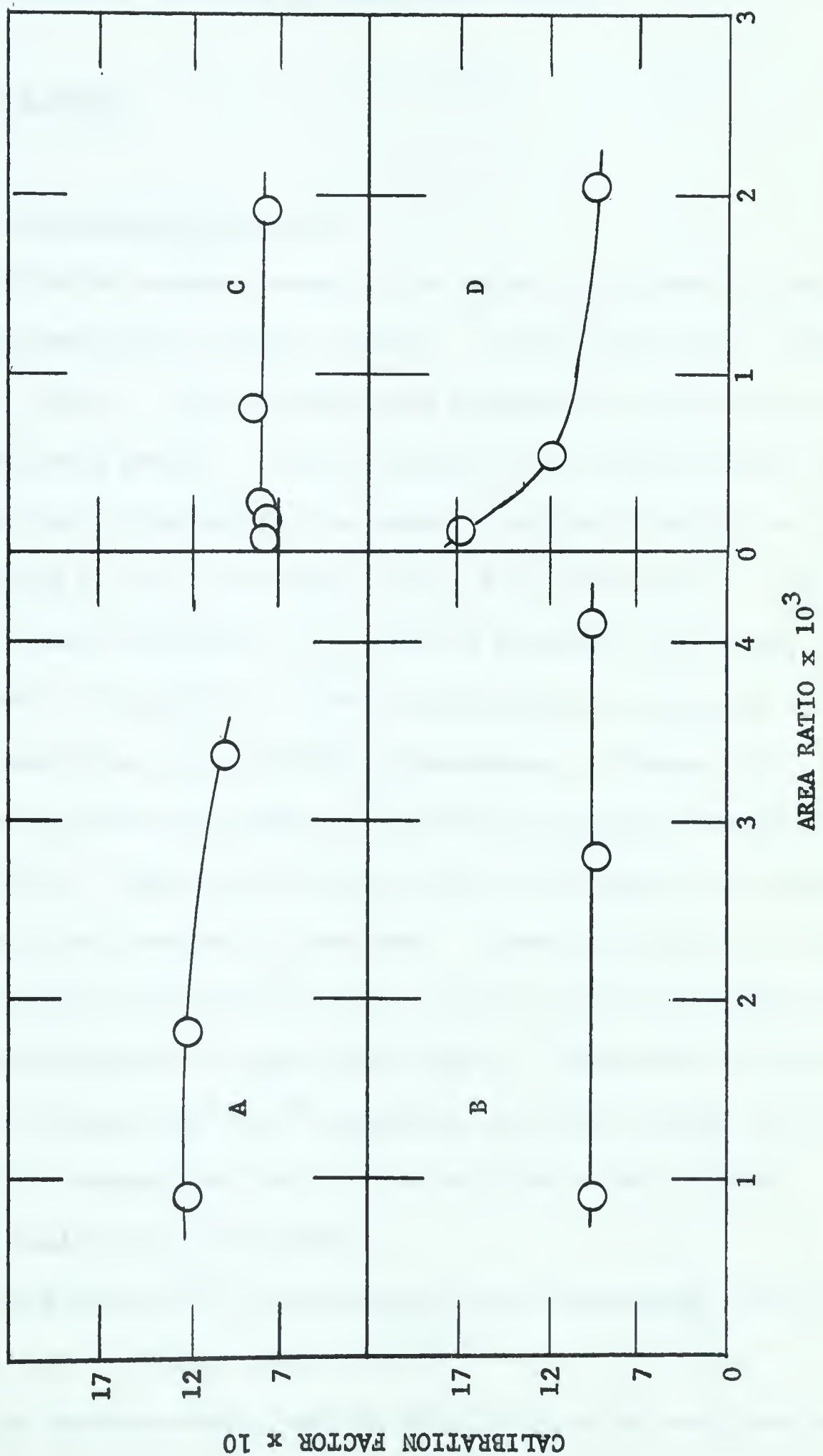
Compound: Ethyl i-propyl ether
Column: Silicone grease

C

Compound: Ethyl n-propyl ether
Column: Ucon

D

Compound: Acetaldehyde
Column: Di-2 ethyl hexyl sebacate



SECTION III - RESULTS

(A) THE LIQUID PHASE RADIOLYSIS OF LIGHT ETHYL ETHER

(a) Pure Liquid Phase

(1) Major Products ($G > 0.5$)

The major products were, in the order of decreasing G-values, hydrogen, 2,3-diethoxybutane, ethanol, ethane, ethyl vinyl ether, ethylene and s-butyl ethyl ether. 2,3-Diethoxybutane appeared on the chromatogram as two closely overlapping peaks. It was probably the dl- and the meso- forms. Myron (81) found that 2,3-butanediol also behaved similarly and the two peaks were found to be due to the dl- and meso- forms of 2,3-butanediol. The yields are reported in terms of G-values (the number of molecules formed per 100 ev of energy absorbed). The effects of dose on the G-values are given in Table III.1. These data are graphically represented in Figure III.1, 2 and 3. The G-values and the dose ranges of studies for the major products are shown on Table III.2. The initial G-value (G_i) of hydrogen was obtained by extrapolation of the G-values to zero dose. Because of their low concentrations at a dose lower than 4×10^{19} ev/gm, all the products, except hydrogen, cannot be measured accurately at this dose region. Therefore, the true nature of the dose effect between 0 to 4×10^{19} ev/gm was not known, except in the case of hydrogen. For this reason, the initial yields of the other products besides hydrogen could not be determined.

The G-value of 2,3-diethoxybutane was the average value of the data from two g.c. columns (Table III.1).

The chromatographic peak of ethyl vinyl ether could not be

TABLE III.1

G-Values of Major Products as a Function of Dose

<u>Product</u>	<u>G</u>	<u>G.C. Column</u>	<u>Dose</u> <u>$\times 10^{-20}$</u>	<u>Figure</u>
Hydrogen	3.66	Charcoal	0.05	III.1
	3.61	"	0.06	
	3.56	"	0.086	
	3.48	"	0.20	
	3.42	"	0.40	
	3.40	"	0.80	
	3.41	"	1.21	
	3.42	"	1.23	
	3.40	"	3.50	
	3.44	"	4.08	
	3.36	"	5.90	
	3.42	"	8.03	

2,3-Diethoxybutane	2.66	Silicone grease	1.03	III.2
	2.76	"	1.59	
	2.52	Ucon	1.59	
	2.74	Silicone grease	2.40	
	2.40	Ucon	2.40	
	2.61	Silicone grease	3.08	
	2.62	"	5.44	

Ethanol	2.1	Ucon	0.514	III.2
	2.0	"	1.03	
	2.28	"	1.70	
	2.16	"	2.10	
	1.93	"	3.08	
	2.32	"	5.44	

Ethane	1.29	Silica gel	0.078	III.3
	1.34	"	0.161	
	1.30	"	0.398	
	1.30	"	1.00	
	1.10	"	1.59	
	1.28	"	2.40	
	1.39	"	2.88	
	1.15	"	3.86	

TABLE III.1 (cont'd)

<u>Product</u>	<u>G</u>	<u>G.C. Column</u>	<u>Dose</u> <u>x10⁻²⁰</u>	<u>Figure</u>
Ethyl vinyl ether	1.2	Tetraethylene glycol dimethyl ether and Ucon	8.4	III.2
	1.1	"	14	
	1.2	"	16.7	
	1.1	"	22	
	1.05	"	22.6	

Ethylene	1.1	Silica gel	0.078	III.3
	0.99	"	0.161	
	0.94	"	0.398	
	0.81	"	1.00	
	0.72	"	1.59	
	0.68	"	2.40	
	0.64	"	2.88	
	0.57	"	3.86	

s-Butyl ethyl ether	0.77	Silicone grease	0.28	III.2
	0.73	Ucon	0.84	
	0.73	"	1.41	
	0.74	"	2.27	
	0.71	Silicone grease	3.5	
	0.77	"	5.44	

TABLE III.2G-Values of Major Products (Average)

<u>Compound</u>	<u>G</u>	<u>Dose Range</u> <u>$\times 10^{-20}$</u>
Hydrogen	3.7 ± 0.1 (G_i) 3.41 ± 0.02	0 0.4-8.0
2,3-Diethoxybutane	2.63 ± 0.23	1.0-5.50
Ethanol	2.13 ± 0.20	0.54-5.5
Ethane	1.27 ± 0.17	0.08-3.9
Ethyl vinyl ether	1.13 ± 0.1	8-23
Ethylene	1.1 to 0.6	0.8-3.9
s-Butyl ethyl ether	0.74 ± 0.03	0.28-5.50

FIGURE III.1

The Dose Dependence of $G(H_2)$

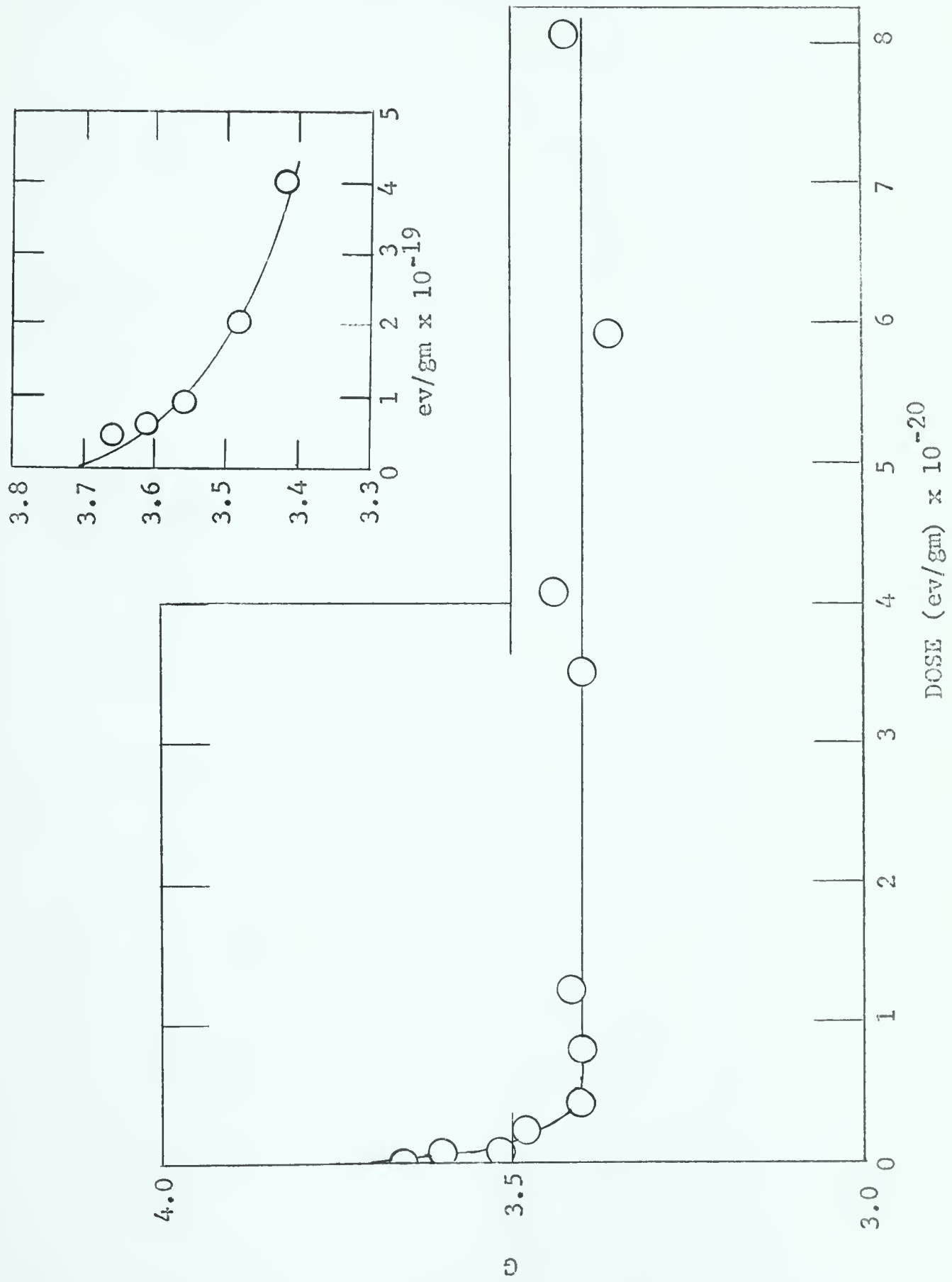


FIGURE III.2The Dose Dependence of Product YieldsA

○ 2,3-Diethoxybutane, silicone
grease column

● 2,3-Diethoxybutane, ucon column

□ Ethanol

△ s-Butyl ethyl ether

B

○ Ethyl vinyl ether

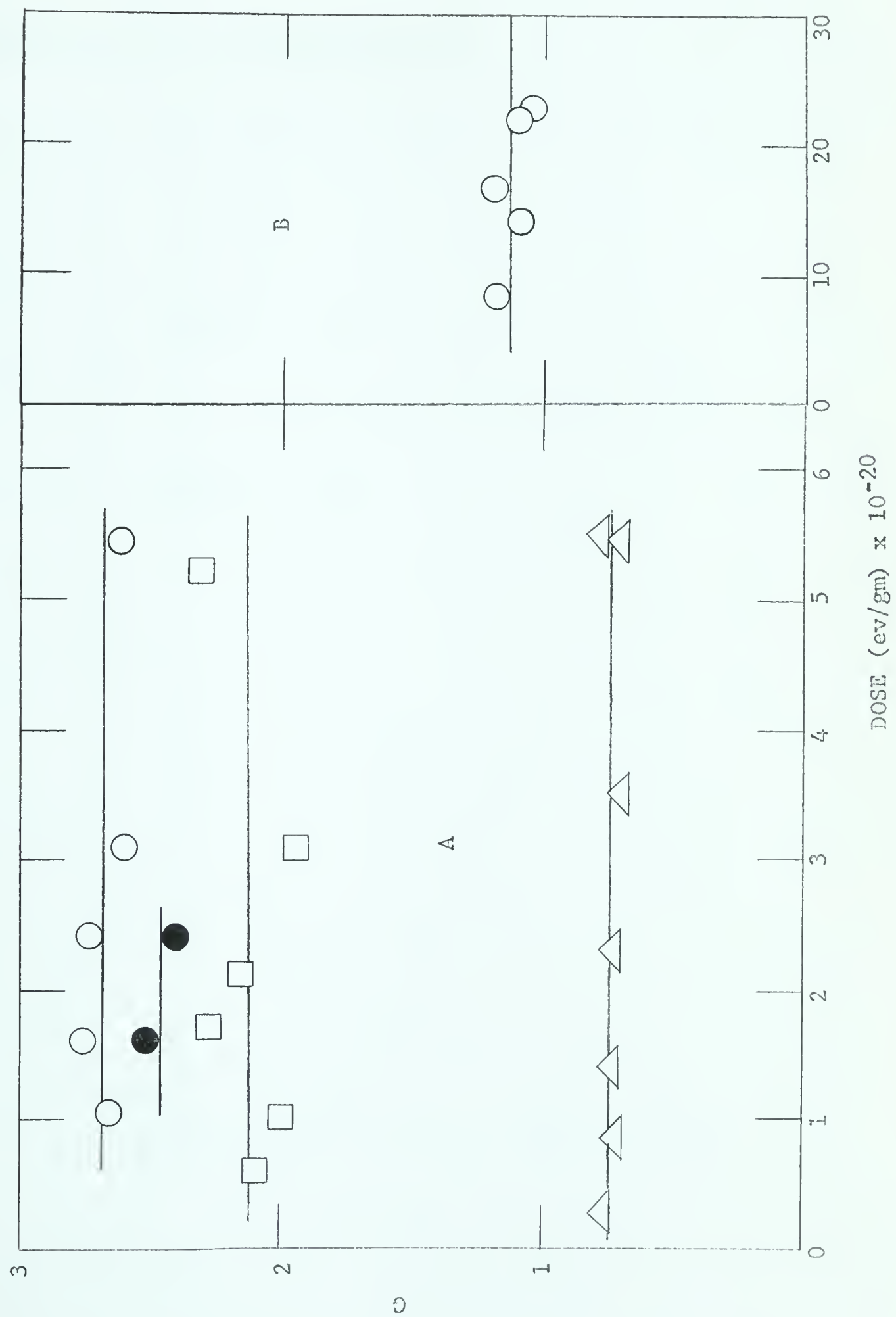
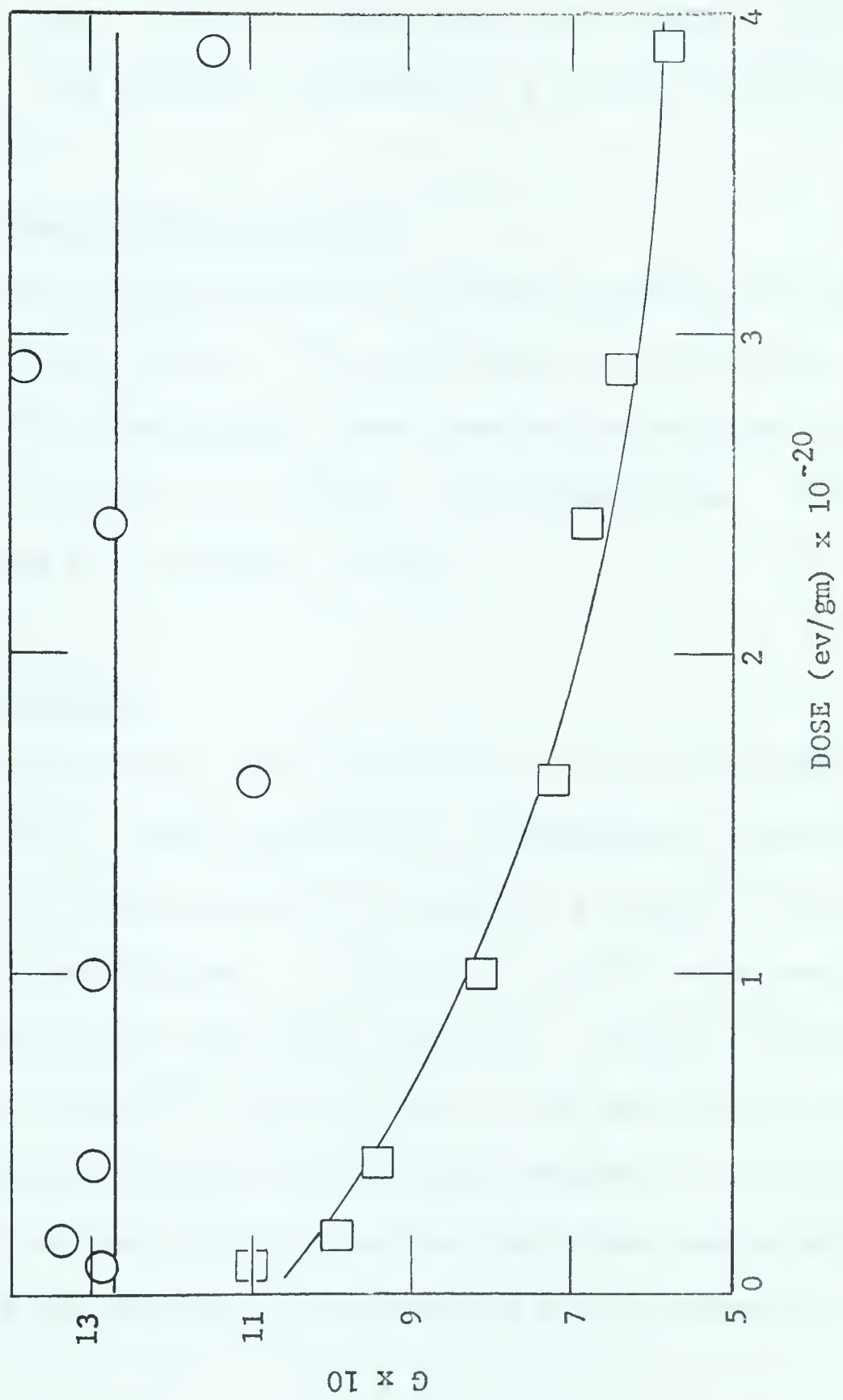


FIGURE III.3The Dose Dependence of Product Yields

○ Ethane

□ Ethylene



observed at a dose $< 8 \times 10^{20}$ ev/gm because of poor separation from the substrate peak. When solutions having 0.15% of ethyl vinyl ether in ethyl ether were radiolyzed, the percentage of ethyl vinyl ether was found to increase as a linear function of dose from 0.5 to 2.9×10^{20} ev/gm (Table III.4, Figure III.4). This increase corresponds to a G unit of 1.1 ± 0.25 .

(2) Minor Products ($G < 0.5$)

The average G-values for the minor products are shown on Table III.3. The dose ranges of the measurements are also given.

Two chromatographic peaks remained unidentified (Table III.3). One of the unknown products was probably 1,3-diethoxybutane. The other was probably formed by a secondary reaction.

(b) Additive Studies

Three compounds were used as additives in the liquid phase radiolysis of ethyl ether. They were benzene, 1,3-pentadiene, and ethyl vinyl ether. The yield of each product was studied as a function of the electron fraction, ϵ_a , of the additives. A dose of $7 \pm 1 \times 10^{19}$ ev/gm was used for the benzene and the ethyl vinyl ether solutions. For the 1,3-pentadiene solutions a dose of 3.5×10^{20} ev/gm was used for the gas products analysis, and 1.0×10^{21} ev/gm was used for liquid product analysis. In all Figures, the dotted lines represent the G-values that would have been expected if the additives had not influenced the radiolysis of the substrate.

(1) Hydrogen

The results are given on Table III.5 and Figure III.5. The hydrogen yield was protected in all cases. The effectiveness was

TABLE III.3Average G-values of Minor Products

<u>Compound</u>	<u>G</u>	<u>Dose Range</u> <u>$\times 10^{-20}$</u>
Methane	0.41 ± 0.03	0.7-3.6
Acetaldehyde	0.18 ± 0.03	3-5
Acetal	0.14 ± 0.03	3-10
1,2-Diethoxypropane	~ 0.09	4-17
1,2-Diethoxyethane	0.08 ± 0.03	1-3
Propane	0.078 ± 0.004	0.39-2.9
Diethoxymethane	0.075 ± 0.007	3-10
Ethyl i-propyl ether	0.074 ± 0.003	1.5-3.5
Carbon monoxide	0.07 ± 0.008	0.7-3.6
Ethyl n-propyl ether	0.059 ± 0.003	0.8-2.3
Butane	0.053 ± 0.005	0.39-2.9
n-Butyl ethyl ether	0.031 ± 0.004	3-10
Acetylene	0.013 ± 0.001	0.39-2.9
Unknown ₂	~ 0.16	4-17
Unknown ₁	~ 0.09	4-17

TABLE III.4The Dose Dependence of the Concentration of Ethyl Vinyl Ether

(Initial concentration = 0.15% by weight)

<u>Concentration by Weight</u>	<u>Dose x 10⁻²⁰</u>
0.15	0
0.154	0.45
0.57	0.72
0.1545	0.92
0.171	1.47
0.166	1.7
0.175	2.08
0.178	2.5
0.178	2.64
0.196	2.9

FIGURE III.4

The Dose Dependence of the Concentration of Ethyl Vinyl Ether

(Initial concentration = 0.15% by weight)

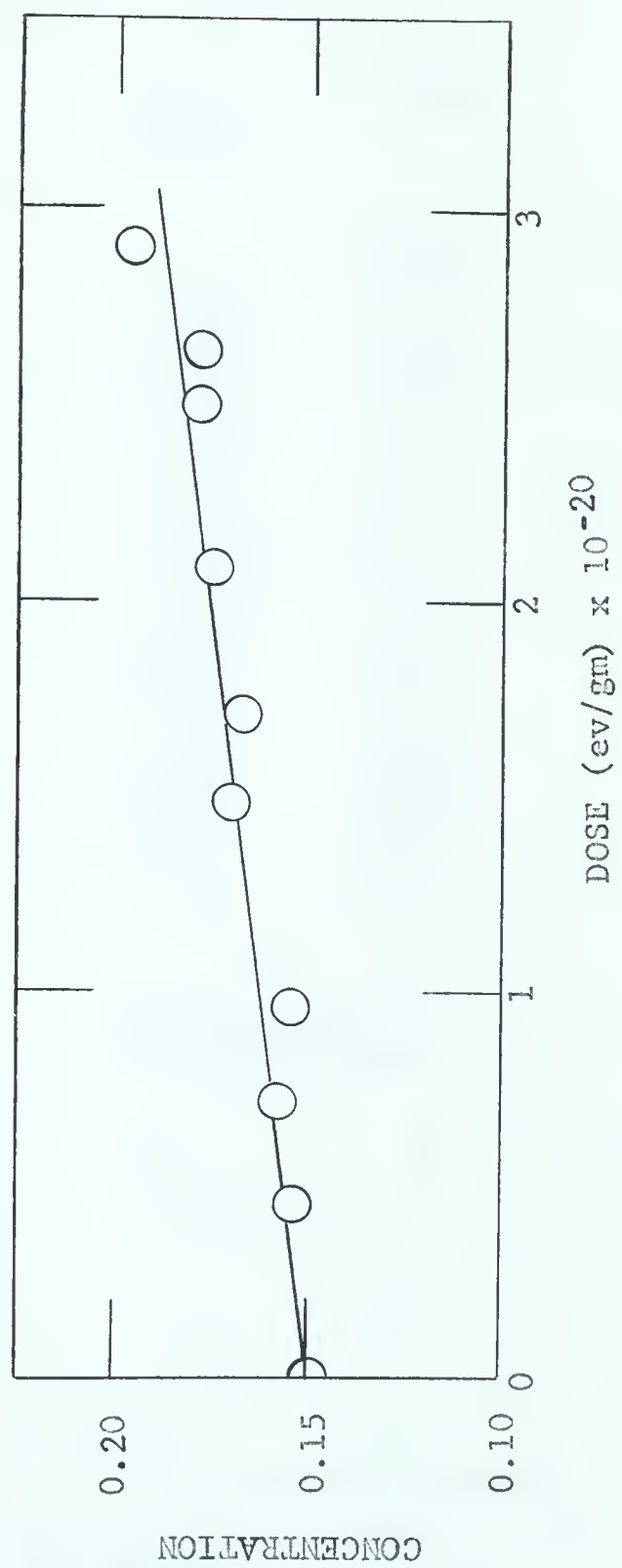


TABLE III.5

Influence of Additives on Product Yields

<u>A</u>					
<u>G(H₂)</u>					
<u>€_B^a</u>	<u>G</u>	<u>€_V^b</u>	<u>G</u>	<u>€_P^c</u>	<u>G</u>
0	3.40	0	3.40	0	3.40
0.032	3.03	0.0008	3.35	0.06	1.32
0.043	3.03	0.0023	3.25	0.13	1.07
0.069	2.81	0.0062	3.03	0.235	0.73
0.091	2.50	0.0099	2.79		
0.169	1.95	0.0153	2.67		
0.211	1.81	0.016	2.63		
0.471	0.074	0.0304	2.39		
0.619	0.50	0.0496	2.06		
1.00	0.038	0.0785	1.75		
		0.246	1.26		
		0.367	1.04		
		0.468	0.93		
		0.635	0.72		
		1.0	0.52		

<u>B</u>					
<u>G(CH₃CHOC₂H₅)₂</u>					
<u>€_B</u>	<u>G</u>	<u>€_V</u>	<u>G</u>	<u>€_P</u>	<u>G</u>
0	2.63			0	2.63
0.036	2.40			0.015	0.12
0.093	1.6			0.04	0.11
0.214	0.72			0.13	0.01
0.35	0.36				

a: subscript B stands for benzene

b: subscript V stands for ethyl vinyl ether

c: subscript P stands for 1,3-pentadiene

TABLE III.5 (cont'd)

<u>C</u>		<u>G(C₂H₅OH)</u>			
<u>€_B</u>	<u>G</u>	<u>€_V</u>	<u>G</u>	<u>€_P</u>	<u>G</u>
0	2.13	0	2.13	0	2.13
0.056	1.64	0.03	1.49	0.015	1.12
0.071	1.45			0.04	0.98
0.201	0.96			1.0	0.0
0.365	0.75				
0.454	0.49				
0.627	0.32				
1.0	0.0				

<u>D</u>		<u>G(C₂H₆)</u>			
<u>€_B</u>	<u>G</u>	<u>€_V</u>	<u>G</u>	<u>€_P</u>	<u>G</u>
0	1.27	0	1.27	0	1.27
0.028	1.02	0.0274	1.1	0.06	0.17
0.084	0.84	0.091	0.8	0.13	0.09
0.335	0.44	0.316	0.54	0.235	0.04
0.57	0.215	0.615	0.435		
1.0	0.00	1.0	0.146		

<u>E</u>		<u>G(C₂H₄)</u>			
<u>€_B</u>	<u>G</u>	<u>€_V</u>	<u>G</u>	<u>€_P</u>	<u>G</u>
0	0.86	0	0.84	0	0.6
0.028	0.69	-	-	0.06	0.41
0.084	0.56	0.027	0.75	0.13	0.23
0.335	0.24	0.091	0.63	0.235	0.14
0.57	0.12	0.316	0.49		
1.0	0.00	0.615	0.42		
		1.0	0.43		

TABLE III.5 (cont'd)

FG(s-Butyl Ethyl Ether)

<u>€_B</u>	<u>G</u>	<u>€_V</u>	<u>G</u>	<u>€_P</u>	<u>G</u>
		0	0.74	0	0.74
		0.03	0.58	0.015	0.25
				0.04	0.18
				0.13	0.07

GG(CH₄)

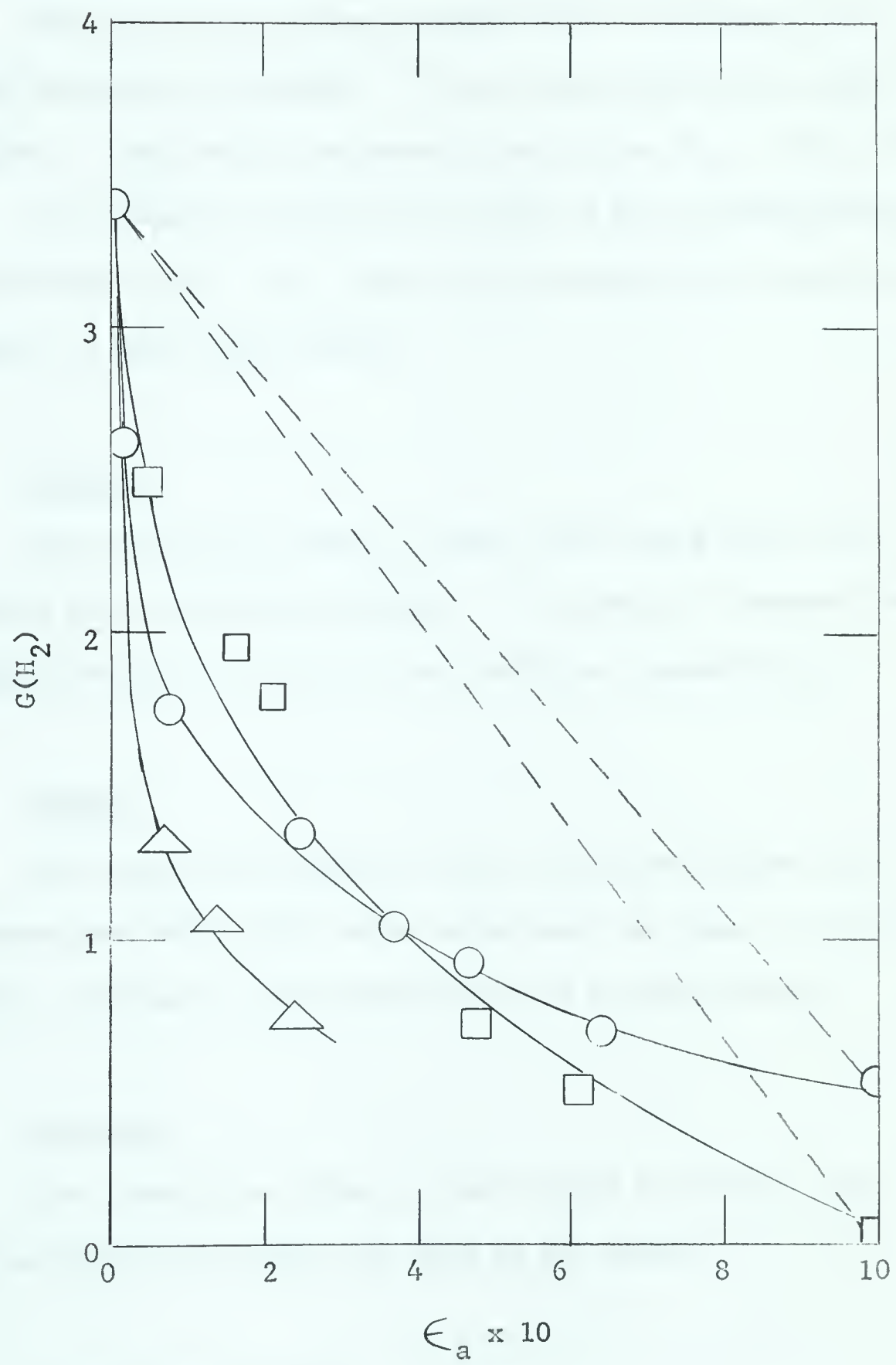
<u>€_B</u>	<u>G</u>	<u>€_V</u>	<u>G</u>	<u>€_P</u>	<u>G</u>
0	0.41	0	0.41	0	0.41
0.336	0.25	0.048	0.37	0.06	0.13
0.618	0.11	0.088	0.29	0.13	0.10
1.0	0.05	0.22	0.23	0.235	0.07
		0.47	0.14		
		1.0	0.05		

HG(CO)

<u>€_B</u>	<u>G</u>	<u>€_V</u>	<u>G</u>	<u>€_P</u>	<u>G</u>
0	0.07	0	0.07	0	0.07
0.029	0.045	0.048	0.085	0.06	0.063
0.336	0.032	0.088	0.097	0.13	0.02
0.618	0.017	0.22	0.094	0.235	0.052
1.0	0.0	0.47	0.096	1.0	0.0
		1.0	0.10		

FIGURE III.5Effect of Additives on $G(H_2)$

	<u>Additive</u>	<u>Dose Range</u> <u>ev/gmx10⁻¹⁹</u>
□	Benzene	6-8
○	Ethyl vinyl ether	6-8
△	1,3-Pentadiene	35



1,3-pentadiene > ethyl vinyl ether > benzene

(2) 2,3-Diethoxybutane

The results are given in Table III.5 and Figure III.9.

The product was protected by benzene. It was very effectively inhibited by 1,3-pentadiene. The G-value decreased from 2.63 at $\epsilon_a = 0.00$ to 0.12 at $\epsilon_a = 0.02$. The effect of ethyl vinyl ether on G(2,3-diethoxybutane) was not studied because the g.c. peak of this compound was covered by peaks of polymers of ethyl vinyl ether.

(3) Ethanol

The results are given in Table III.5 and Figure III.8.

The ethanol yield was protected by benzene. In case of 1,3-pentadiene, $G(C_2H_5OH)$ dropped sharply to ~ 1.0 at low additive concentration.

(4) Ethane

The results are given in Table III.5, and Figure III.7. The effects of benzene and ethyl vinyl ether were about the same. But $G(C_2H_6)$ was drastically inhibited at low concentration of 1,3-pentadiene.

(5) Ethylene

The results are given in Table III.5 and Figure III.7.

The degree of protection was about the same in all cases.

(6) s-Butyl ethyl ether

The results are given in Table III.5 and Figure III.8.

The yield was greatly inhibited at low concentration of 1,3-pentadiene.

FIGURE III.6A. The Effects of Additives on G(CO)

	<u>Additive</u>	<u>Dose Range</u> <u>ev/gmx10⁻¹⁹</u>
□	Benzene	6-8
○	Ethyl vinyl ether	6-8
△	1,3-Pentadiene	35

B. The Effects of Additives on G(CH₄)

	<u>Additive</u>	<u>Dose Range</u> <u>ev/gm x 10⁻¹⁹</u>
□	Benzene	6-8
○	Ethyl vinyl ether	6-8
△	1,3-Pentadiene	35

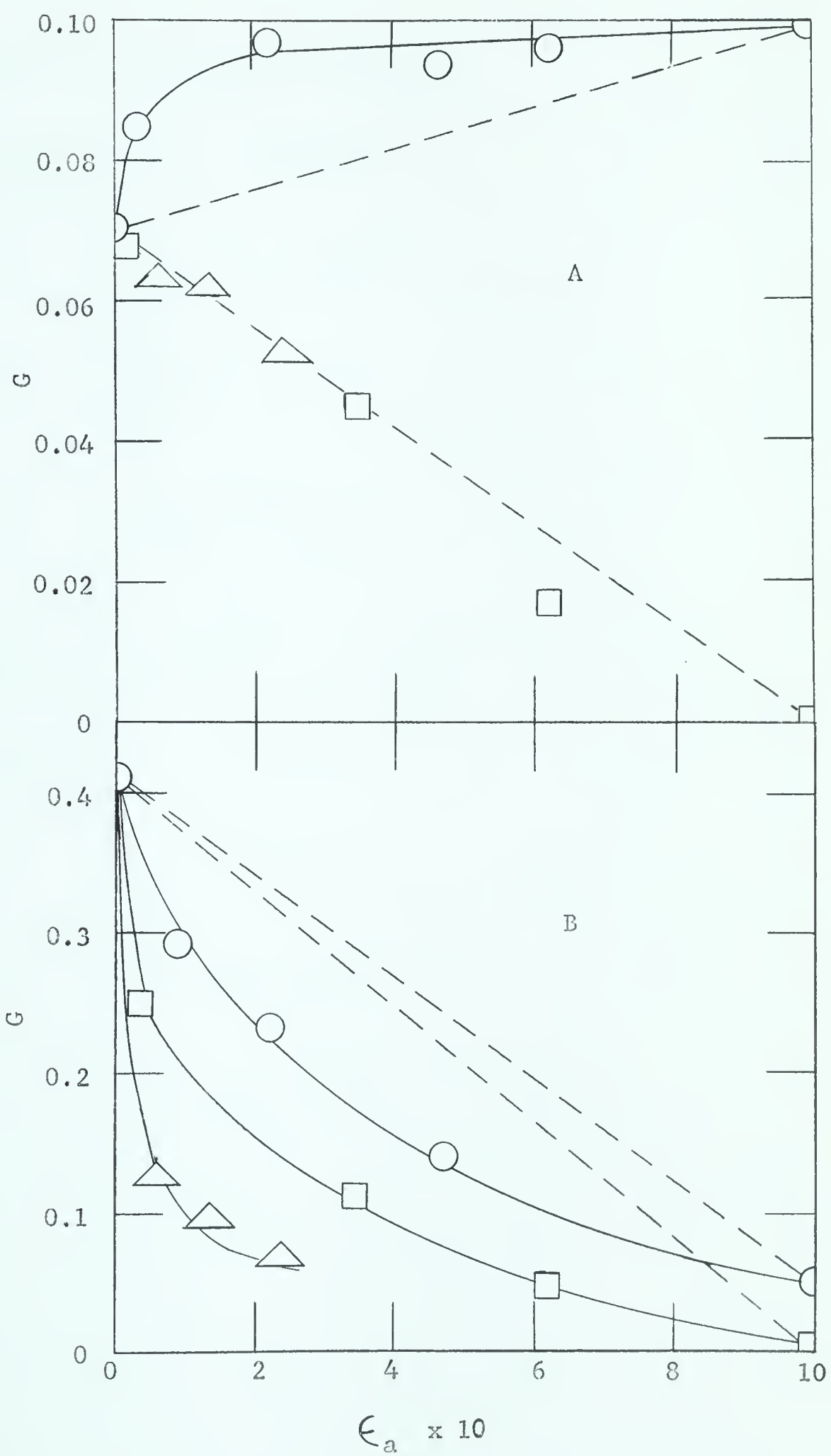








FIGURE III.7A. The Effects of Additives on $G(C_2H_4)$

	<u>Additive</u>	<u>Dose Range</u> <u>ev/gm $\times 10^{-19}$</u>
	Benzene	6-8
	Ethyl vinyl ether	6-8
	1,3-Pentadiene	35

B. The Effects of Additives on $G(C_2H_6)$

	<u>Additive</u>	<u>Dose Range</u> <u>ev/gm $\times 10^{-19}$</u>
	Benzene	6-8
	Ethyl vinyl ether	6-8
	1,3-Pentadiene	35

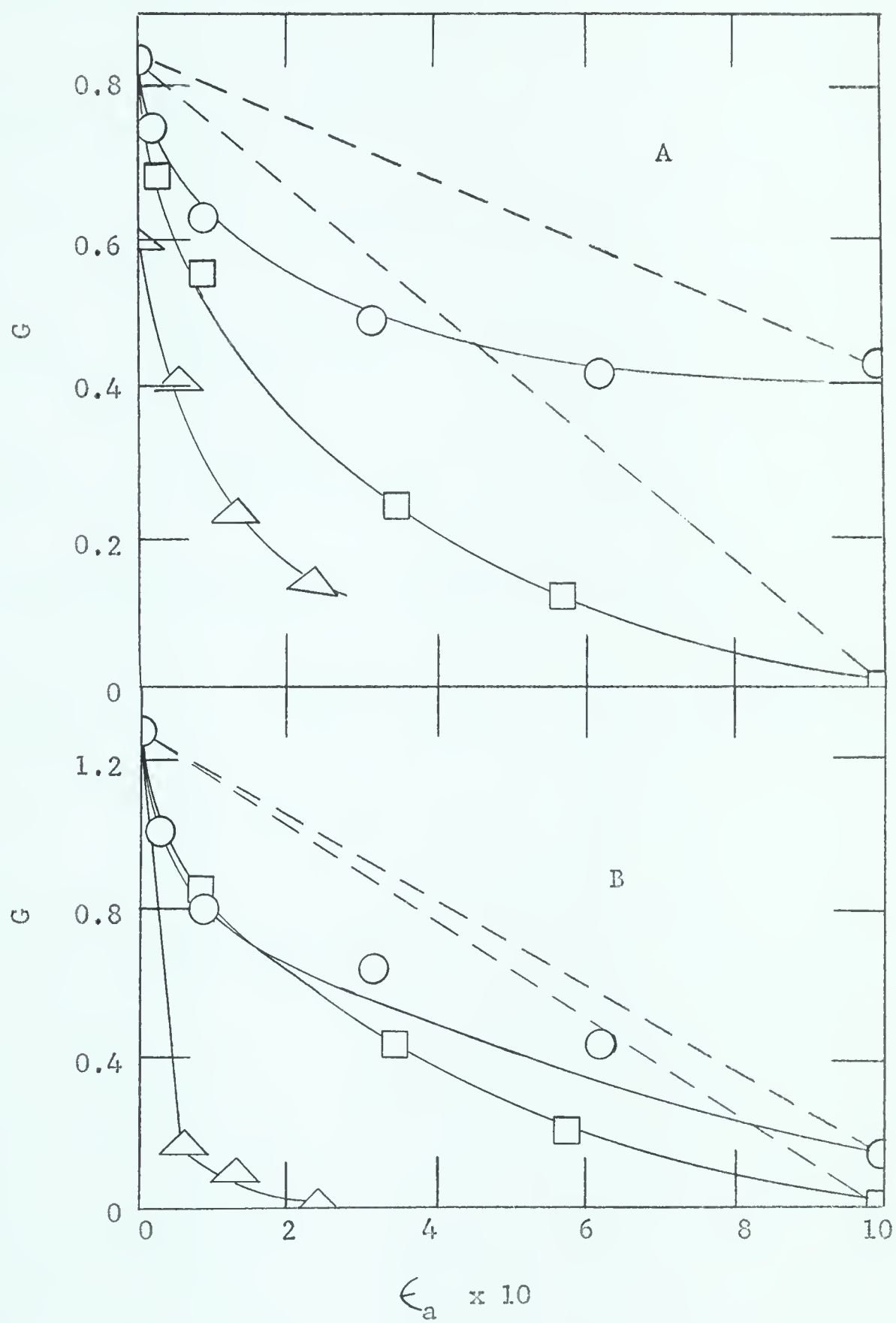







FIGURE III.8A. The Effects of Additives on G(C₂H₅OH)

	<u>Additive</u>	<u>Dose Range</u> <u>ev/gm x 10⁻¹⁹</u>
	Benzene	6-8
	Ethyl vinyl ether	6-8
	1,3-Pentadiene	100

B. The Effects of Additives on G(s-Butyl Ethyl Ether)

	<u>Additive</u>	<u>Dose Range</u> <u>ev/gm x 10⁻¹⁹</u>
	Ethyl vinyl ether	6-8
	1,3-Pentadiene	100

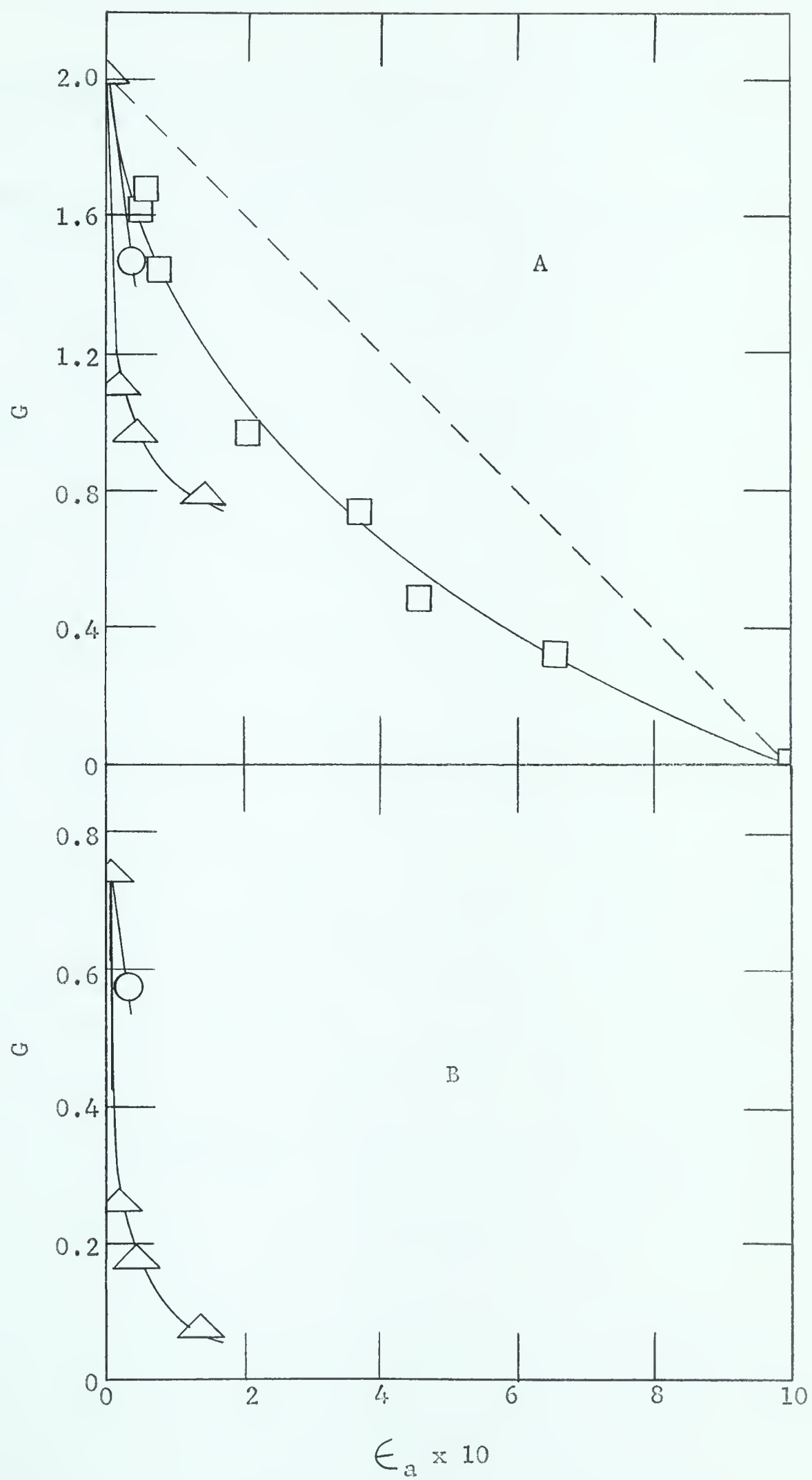


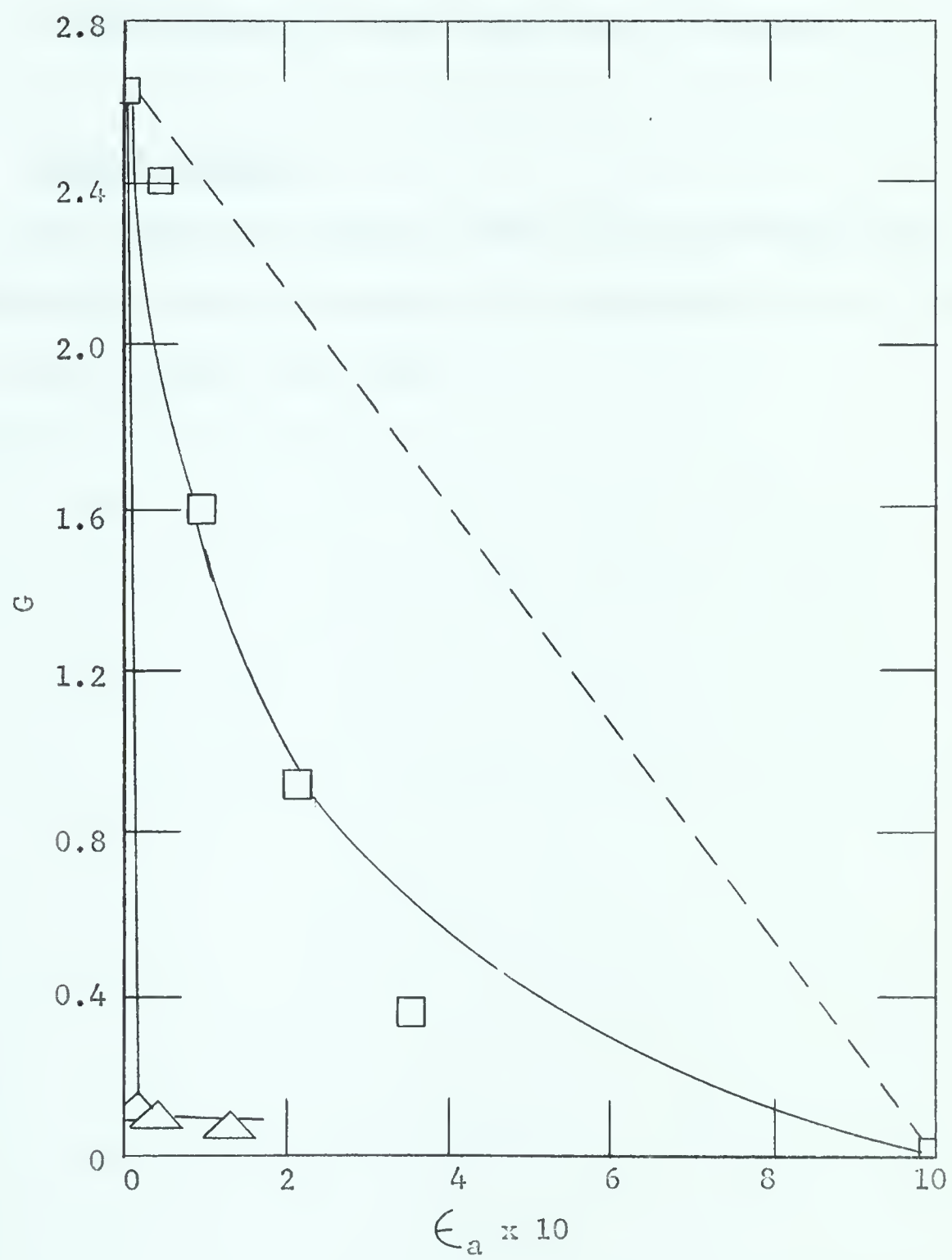


FIGURE III.9The Effects of Additives on G(2,3-Diethoxybutane)

	<u>Additive</u>	<u>Dose Range</u> <u>ev/gm x 10⁻¹⁹</u>
	Benzene	6-8
	1,3-Pentadiene	100



(7) Methane

The results are given in Table III.5 and Figure III.6.

$G(\text{CH}_4)$ was inhibited in all cases. The effectiveness of the additives was

1,3-pentadiene > ethyl vinyl ether > benzene

(8) Carbon Monoxide

The results are given in Table III.5 and Figure III.6.

$G(\text{CO})$ was unaffected in case of benzene and 1,3-pentadiene, but it was sensitized in case of ethyl vinyl ether.

(B) GAS PHASE RADIOLYSIS OF LIGHT ETHYL ETHER

(a) Pure Gas Phase

Three samples were irradiated at a dose of 1×10^{20} , 2×10^{20} , and 3×10^{20} ev/gm respectively. The ether vapor pressure of each sample was about 360 mm. The experiments were carried out at room temperature. The yields of all the products that were found were independent of dose over the region studied. Their average G-values are given in Table III.6.

(b) The Effects of 1,3-Pentadiene

The influence of added 1,3-pentadiene on product yields was studied at a dose of 3.5×10^{20} ev/gm. Three electron fractions of 1,3-pentadiene were used: 0.1, 0.25 and 0.35. The g.c. peaks of all liquid products had disappeared at the lowest concentration of 1,3-pentadiene used. The results of gas product analysis are given in Table III.7 and Figure III. 10 and 11.

TABLE III.6The Average Product Yields in Gas Phase RadiolysisDose Range^a = $1-3 \times 10^{20}$ ev/gm

<u>Product</u>	<u>G</u>
Hydrogen	6.44
2,3-Diethoxybutane	2.38
Ethylene	2.10
Acetaldehyde	1.42
Methane	1.26
Ethyl i-propyl ether	1.00
s-Butyl ethyl ether	0.83
Ethanol	0.65
Ethane	0.44
Carbon monoxide	0.40
Ethyl vinyl ether	0.4
Diethoxymethane	0.22
Propane	0.14
Ethyl methyl ether	0.14
Acetal	0.09
Acetylene	0.03
Formaldehyde	0.9

a: All products are measured at the dose range stated except ethyl vinyl ether and acetaldehyde, which are measured at 1.0×10^{21} ev/gm and 5×10^{20} ev/gm respectively.

TABLE III.7The Effects of 1,3-Pentadiene on the Product Yields in GasPhase RadiolysisDose = 3.5×10^{20} ev/gm

<u>ϵ_p^a</u>	<u>$G(H_2)$</u>	<u>$G(CH_4)$</u>	<u>$G(CO)$</u>	<u>$G(C_2H_6)$</u>	<u>$G(C_2H_4)$</u>
0.0	6.44	1.26	0.40	0.44	2.10
0.086	1.94	0.34	0.32	0.07	1.56
0.228	1.41	0.19	0.28	0.05	1.30
0.322	1.20	0.16	0.22	0.04	1.06

a: ϵ_p stands for the electron fraction of 1,3-pentadiene

FIGURE III.10

Hydrogen Yield as a Function of 1,3-Pentadiene Concentration

(Gas Phase Radiolysis)

$$\text{Dose} = 3.5 \times 10^{20} \text{ ev/gm}$$

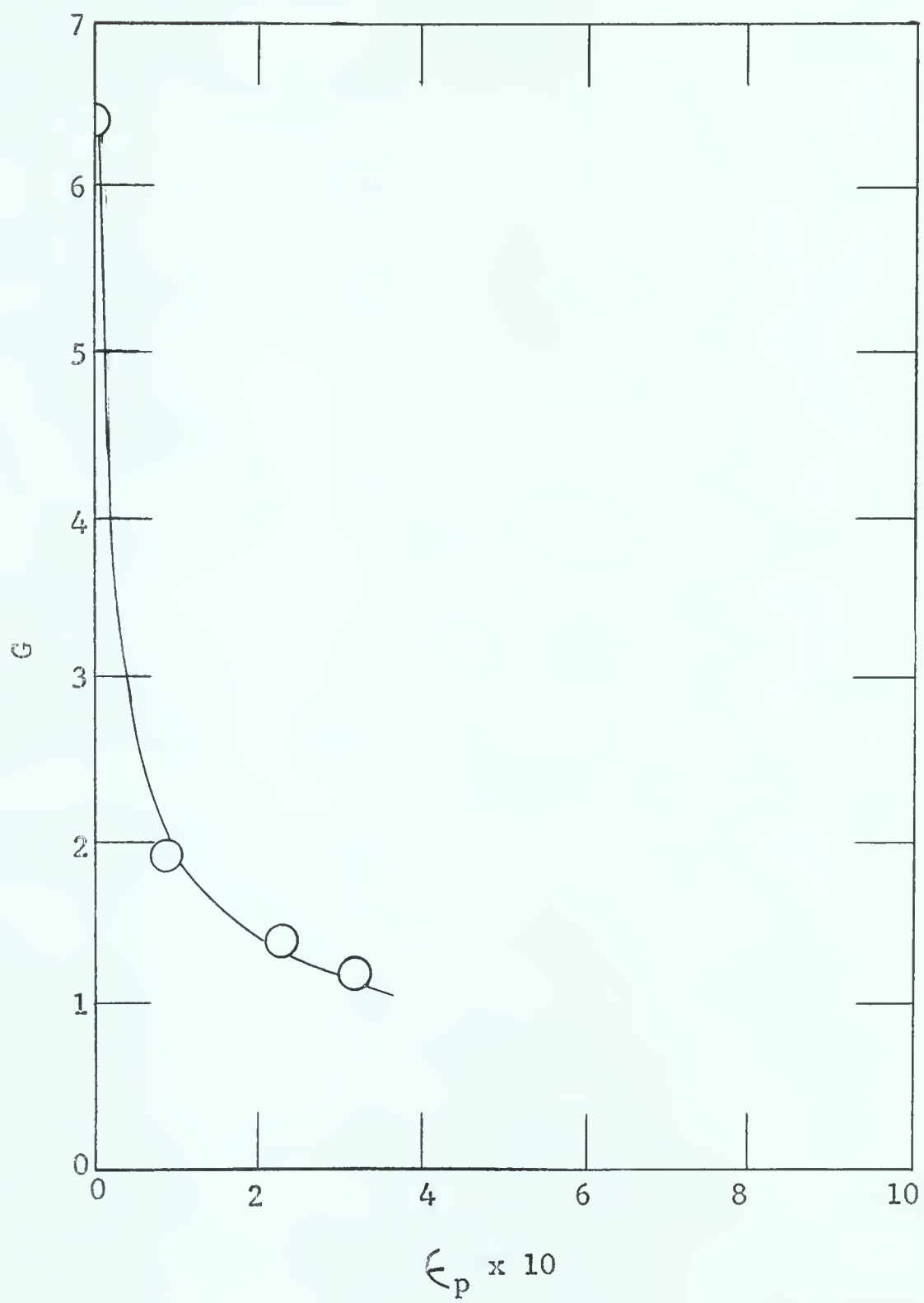


FIGURE III.11

The Product Yields as a Function of 1,3-Pentadiene Concentration

(Gas Phase Radiolysis)

$$\text{Dose} = 3.5 \times 10^{20} \text{ ev/gm}$$

A.



Ethylene



Methane

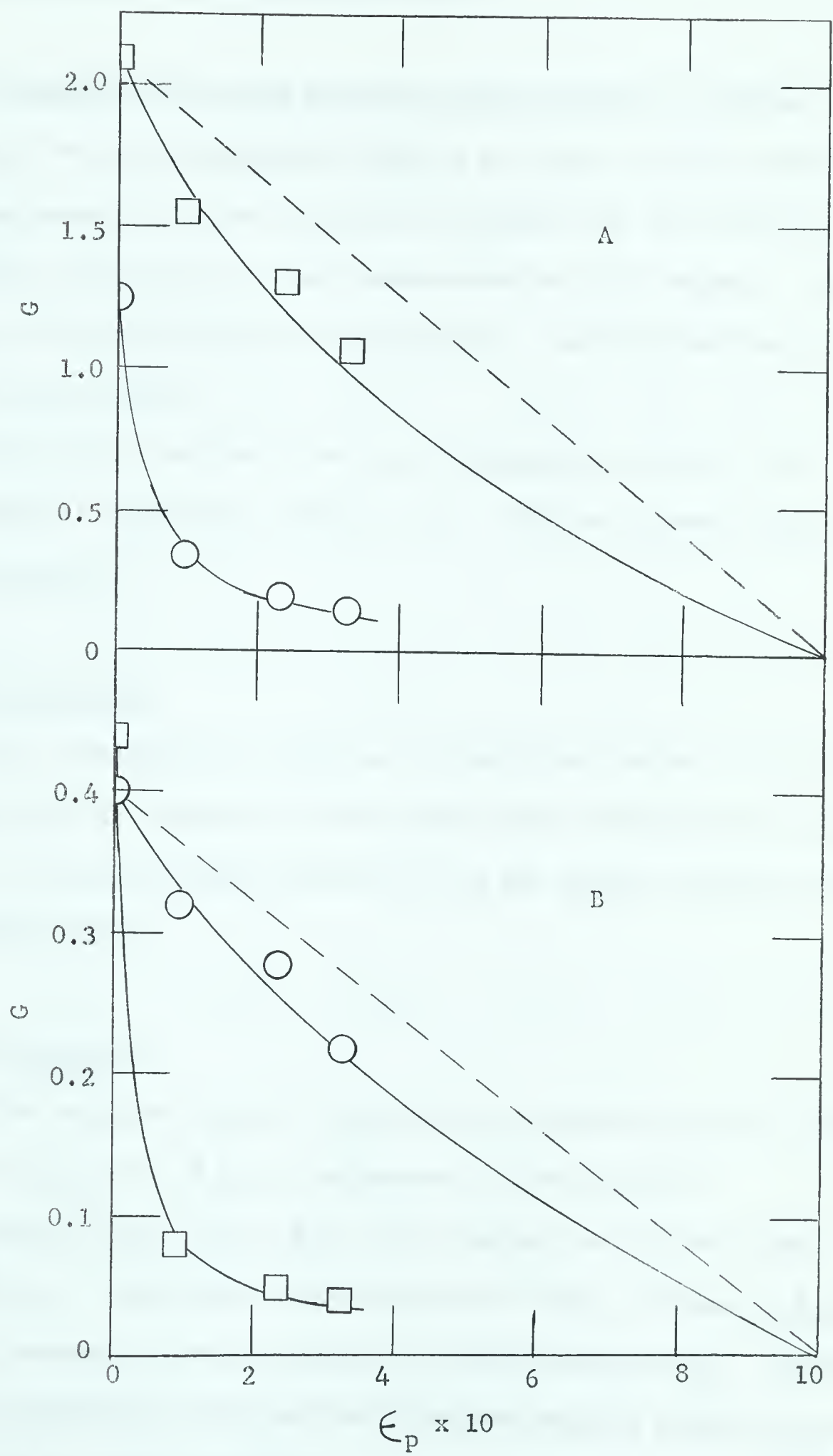
B.



Carbon monoxide



Ethane



(C) RADIOLYSIS OF DEUTERATED ETHYL ETHERS

Radiolysis of three deuterated ethyl ethers — α -d₄, β -d₆, and -d₁₀ — were investigated both in the vapor and the liquid phase. The ether vapor pressure in the gas phase radiolysis was about 360 mm. Experiments were carried out at room temperature for both phases. Their 1,3-pentadiene solutions were also investigated. An electron fraction of 0.17 was used in each case.

The liquid products were not investigated because their g.c. peaks were masked by impurities (Table II.1). The gas products were analysed mass spectrometrically.

(a) -196°C Fraction

The uninhibited as well as the inhibited yields of carbon monoxide, hydrogen, and methane for the liquid phase radiolysis are given in Table III.8. The corresponding values for the gas phase radiolysis are presented in Table III.9.

(b) -155°C Fraction

The relative isotopic composition of ethylene for the radiolysis of ethyl ether- α -d₄ and - β -d₆ is presented in Table III.10.

Ethane C₂H₃D₃ and C₂H₂D₄ were obtained in the radiolysis of ethyl ether- β -d₆. The former was predominant (~60%). Ethane C₂H₃D₃ and C₂H₄D₂ were obtained in the radiolysis of ethyl ether- α -d₄. However, their relative composition could not be determined because ethane C₂H₄D₂ was masked by the air peak (m/e = 32).

TABLE III.8

Product Yields in the Radiolysis of Deuterated Ethyl Ethers

(Liquid Phase)

A. Hydrogen

<u>Ethyl Ether</u>	$\epsilon_P^a = 0$				$\epsilon_P = 0.17$			
	<u>G(H₂)</u>	<u>G(HD)</u>	<u>G(D₂)</u>	<u>G(Hyd)^b</u>	<u>G(H₂)</u>	<u>G(HD)</u>	<u>G(D₂)</u>	<u>G(Hyd)</u>
(C ₂ H ₅) ₂ O	3.42	0	0	3.43	0.92	0	0	0.92
(CD ₃ CH ₂) ₂ O	2.27	0.69	0.076	3.04	0.57	0.211	0.038	0.82
(CH ₃ CD ₂) ₂ O	0.553	1.07	0.52	2.14	0.274	0.292	0.11	0.68
(C ₂ D ₅) ₂ O	0.03	0.09	1.58	1.70	0.07	0.15	0.29	0.51

B. Methane

(1)	$\epsilon_P = 0$					
<u>Ethyl Ether</u>	<u>G(CH₄)</u>	<u>G(CDH₃)</u>	<u>G(CD₂H₂)</u>	<u>G(CD₃H)</u>	<u>G(CD₄)</u>	<u>G(Methane)</u>
(C ₂ H ₅) ₂ O	0.417	0	0	0	0	0.417
(CD ₃ CH ₂) ₂ O	0.068	0.039	0.033	0.237	0.018	0.395
(CH ₃ CD ₂) ₂ O	0.189	0.175	0.011	0	0	0.375
(C ₂ D ₅) ₂ O	0.017	0.019	0	0.054	0.41	0.50

a: ϵ_P stands for the electron fraction of 1,3-pentadieneb: $G(\text{Hyd}) = G(\text{H}_2) + G(\text{HD}) + G(\text{D}_2)$

TABLE III.8 (cont'd)

(2) $\epsilon_p = 0.17$						
<u>Ethyl Ether</u>	<u>G(CH₄)</u>	<u>G(CDH₃)</u>	<u>G(CD₂H₂)</u>	<u>G(CD₃H)</u>	<u>G(CD₄)</u>	<u>G(Methane)</u>
(C ₂ H ₅) ₂ O	0.086	0	0	0	0	0.086
(CD ₃ CH ₂) ₂ O	0.009	0.007	0.006	0.036	0.005	0.063
(CH ₃ CD ₂) ₂ O	0.034	0.03	0.003	0	0	0.067
(C ₂ D ₅) ₂ O	0.009	0	0	0.022	0.038	0.069

C. Carbon Monoxide

<u>Ethyl Ether</u>	<u>G(CO) ($\epsilon_p = 0$)</u>	<u>G(CO) ($\epsilon_p = 0.17$)</u>
(C ₂ H ₅) ₂ O	0.073	0.058
(CD ₃ CH ₂) ₂ O	0.09	0.054
(CH ₃ CD ₂) ₂ O	0.053	0.032
(C ₂ D ₅) ₂ O	0.094	0.036

TABLE III.9

Product Yields in the Radiolysis of Deuterated Ethyl Ethers

(Gas Phase)

A. Hydrogen

<u>Ethyl Ether</u>	$\epsilon_P^a = 0$				$\epsilon_P = 0.17$			
	<u>G(H₂)</u>	<u>G(HD)</u>	<u>G(D₂)</u>	<u>G(Hyd)^b</u>	<u>G(H₂)</u>	<u>G(HD)</u>	<u>G(D₂)</u>	<u>G(Hyd)</u>
(C ₂ H ₅) ₂ O	6.44	0	0	6.44	1.64	0	0	1.64
(CD ₃ CH ₂) ₂ O	4.40	1.47	0.14	6.01	1.00	0.32	0.08	1.40
(CH ₃ CD ₂) ₂ O	1.18	1.90	0.72	3.80	0.494	0.44	0.12	1.05
(C ₂ D ₅) ₂ O	0.10	0.08	3.07	3.25	0.18	0.26	0.29	0.37

B. Methane

(1)	$\epsilon_P = 0$					
<u>Ethyl Ether</u>	<u>G(CH₄)</u>	<u>G(CDH₃)</u>	<u>G(CD₂H₂)</u>	<u>G(CD₃H)</u>	<u>G(CD₄)</u>	<u>G(Methane)</u>
(C ₂ H ₅) ₂ O	1.25	0	0	0	0	1.25
(CD ₃ CH ₂) ₂ O	0.164	0.119	0.102	0.750	0.051	1.186
(CH ₃ CD ₂) ₂ O	0.213	0.179	0.026	0	0	0.418
(C ₂ D ₅) ₂ O	0.14	0.11	0	0.23	1.43	1.910

a: ϵ_P stands for the electron fraction of 1,3-pentadieneb: $G(\text{Hyd}) = G(\text{H}_2) + G(\text{HD}) + G(\text{D}_2)$

TABLE III.9 (cont'd)

(2)	$\epsilon_p = 0.17$					
<u>Ethyl Ether</u>	<u>G(CH₄)</u>	<u>G(CDH₃)</u>	<u>G(CD₂H₂)</u>	<u>G(CD₃H)</u>	<u>G(CD₄)</u>	<u>G(Methane)</u>
(C ₂ H ₅) ₂ O	0.25	0	0	0	0	0.25
(CD ₃ CH ₂) ₂ O	0.038	0.019	0.018	0.114	0.009	0.198
(CH ₃ CD ₂) ₂ O	0.047	0.069	0.009	0.002	0	0.127
(C ₂ D ₅) ₂ O	0.057	0	0	0.505	0.175	0.737

C. Carbon Monoxide

<u>Ethyl Ether</u>	<u>G(CO)</u> <u>($\epsilon_p = 0$)</u>	<u>G(CO)</u> <u>($\epsilon_p = 0.17$)</u>
(C ₂ H ₅) ₂ O	0.389	0.30
(CD ₃ CH ₂) ₂ O	0.41	0.272
(CH ₃ CD ₂) ₂ O	0.326	0.216
(C ₂ D ₅) ₂ O	1.14	0.144

TABLE III.10

Per Cent Isotopic Composition of Ethylene

<u>Ethyl Ether</u>	<u>Phase</u>	<u>ϵ_p^a</u>	<u>C₂H₄</u>	<u>C₂H₃D</u>	<u>C₂H₂D₂</u>	<u>C₂HD₃</u>
(CD ₃ CH ₂) ₂ O	liquid	0	7.3	13.9	51.6	27.2
(CD ₃ CH ₂) ₂ O	liquid	0.17	9.4	12.6	46.7	31.3
(CH ₃ CD ₂) ₂ O	liquid	0	0	28	72	0
(CH ₃ CD ₂) ₂ O	liquid	0.17	0	26.5	73.5	0
<hr/>						
(CD ₃ CH ₂) ₂ O	gas	0	6.9	12.1	57.4	23.6
(CD ₃ CH ₂) ₂ O	gas	0.17	11.8	11.3	53.8	23.1
(CH ₃ CD ₂) ₂ O	gas	0	5.3	15.1	75.1	4.5
(CH ₃ CD ₂) ₂ O	gas	0.17	5.6	22.4	69.9	2.1

SECTION IV - DISCUSSION

(A) LIQUID PHASE

(a) Material Balance

A mass balance of all the products observed (Table IV.1) was done at a dose of 1×10^{20} ev/gm, since the yields of most of the products could not be ascertained at lower doses. It was found that ether decomposes with a G value of ~ 11.3 . The reaction products add up to an empirical formula of $C_2H_{10.07}O_{.975}$. The good balance shows that most of the products have probably been accounted for.

(b) C-H Bond Cleavage

The primary C-H bond cleavage, per bond, is given by

$$G(C-H) \text{ per bond} = G(H_2)/10 = 0.37 \text{ -----IV.1}$$

The presence of s-butyl ethyl ether ($G=0.74$) and n-butyl ethyl ether ($G=0.03$) indicates that the C-H cleavage occurs at both α - and β -positions. The α - and β -radicals can be formed by the unimolecular decomposition of an ether molecule (reaction IV.2 and IV.3) as well as by radical abstraction (reaction IV.4 and IV.5).

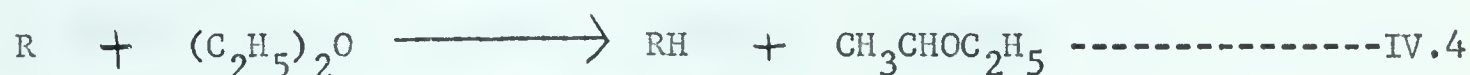
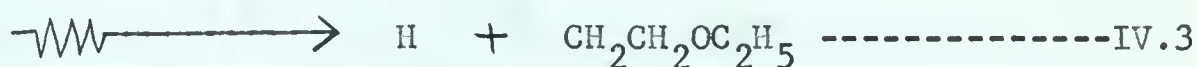
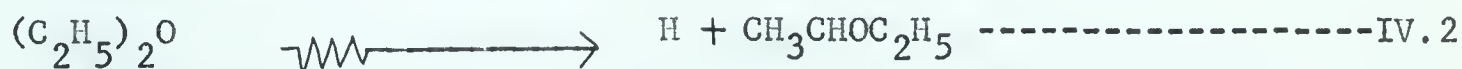


TABLE IV.1

Material Balance For Liquid Ether Radiolysis

<u>Product</u>	<u>C</u>	<u>H</u>	<u>O</u>
H ₂	0	6.8	0
(CH ₃ CHOC ₂ H ₅) ₂	21.0	47.3	5.26
C ₂ H ₅ OH	4.26	12.8	2.13
C ₂ H ₆	2.45	7.35	0
C ₂ H ₄	1.8	3.6	0
C ₂ H ₃ OC ₂ H ₅	4.52	9.04	1.13
C ₂ H ₅ OCH(CH ₃)C ₂ H ₅	4.44	10.36	.74
CH ₄	0.41	1.64	0
C ₃ H ₈	0.23	0.62	0
C ₂ H ₅ OC ₃ H ₇	0.30	0.71	0.06
C ₂ H ₅ OCH(CH ₃) ₂	0.37	0.89	0.07
C ₂ H ₅ OCH(CH ₃)CH ₂ OC ₂ H ₅	0.63	1.44	0.18
CH ₂ (OC ₂ H ₅) ₂	0.375	0.90	0.15
(CH ₂ OC ₂ H ₅) ₂	0.48	1.12	0.16
CO	0.07	0	0.07
C ₄ H ₉ OC ₂ H ₅	0.08	0.43	0.03
C ₄ H ₁₀	0.21	0.53	0
C ₂ H ₂	0.03	0.03	0
CH ₃ CH(OC ₂ H ₅) ₂	0.84	1.96	0.28
CH ₃ CHO	0.32	0.72	0.18
Unknown 1 and 2 ^a	2.0	4.5	0.5
Total	44.48	112.7	10.9

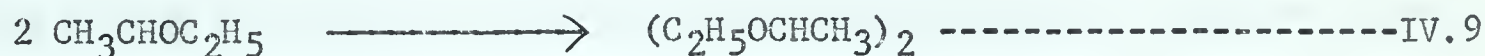
a: Unknown 1 and 2 are assumed to be C₈H₁₈O₂.



If reactions IV.6 and IV.7 have the same rate constant, one can calculate the ratio of the probabilities of formation of the α - and β -radicals²

$$\frac{[\alpha\text{-radical}]}{[\beta\text{-radical}]} = \frac{G(C_2H_5OCH(CH_3)C_2H_5)}{G(C_2H_5OC_4H_9)} = 25 \text{ -----IV.8}$$

This gives the relative probability of breaking an α C-H to that of breaking a β -H. This shows that the overall C-H bond cleavage occurs preferentially at the α -position. This preference is also supported by the large yield of the dimer 2,3-diethoxybutane ($G=2.67$) which is formed by the combination of two α -radicals:



No 1,4-dimer was found. The 1,3-dimer might correspond to one of the unidentified peaks, unknown 1 ($G=0.09$) (Page 61).



a: α and β radicals refer to $CH_3CHOC_2H_5$ and $CH_2CH_2OC_2H_5$ respectively.

If this is true, and if the two dimer forming reactions have the same rate constant, then, again, one can calculate the approximate ratio of the rate of hydrogen loss from the α - and β - positions:

$$\frac{\text{Probability of } \alpha\text{-C-H cleavage}}{\text{Probability of } \beta\text{-C-H cleavage}} = \frac{2G(2,3\text{-dimer})}{G(1,3\text{-dimer})} = 60 \text{ -----IV.11}$$

In view of the small and therefore inaccurately measured yield of n-butyl ethyl ether and 1,3-dimer, the ratios obtained from equations IV.8 and IV.11 are in reasonable agreement. The ratios give an average value of 40.

If the different reactivities of the two hydrogen sites are attributed to the difference in activation energy, ΔE , in the abstraction reactions, then ΔE can be estimated from the following expression:

$$\frac{3}{2} \times \frac{R_{\alpha}}{R_{\beta}} = 60 = \exp(\Delta E/RT) \text{ -----IV.12}$$

$$\therefore \Delta E = 2.4 \text{ kcal mole}^{-1}$$

where R_{α} is the rate of α -H loss, etc. The factor 3/2 is included because there are three β -C-H bonds and two α -C-H bonds.

It is estimated that $D(\alpha\text{-C-H})$ in ether is equal to 94 kcal mole⁻¹ (81)(82). Since this value is similar to $D(\text{C-H})$ for the secondary C-H bond in propane (83)(86), Walling (81) suggested that the ethoxy group and methyl group had the same resonance stabilization effect. In the mercury photosensitized decomposition of propane (84), the per bond ratio of the formation of isopropyl radicals to propyl radicals is equal to 45. Gunning (84) concluded that the secondary C-H bond cleavage was 58% of the total C-H cleavage in the primary quenching reaction. The apparent high percentage of i-propyl radi-

cals was attributed to secondary reactions. This ratio has a value of 15 in the γ -radiolysis of propane (85). Since these ratios (45 and 15) are similar to the ratio R_α/R_β in ether, it seems that the ethoxy and the methyl group do have similar effect on the methylene group, in agreement with Walling's conclusion. The bond dissociation energy for β -C-H cleavage is not known. However, it is probably 6 kcal mole⁻¹ higher than $D(\alpha\text{-C-H})$, such as it is in propane (86).

(c) C-C and C-O Bond Cleavage

The relative probability of C-O bond cleavage, per bond, is given by

$$\begin{aligned} G(\text{C-O}) \text{ per bond} &= \frac{1}{2} \left\{ G(\text{C}_2\text{H}_6) + G(\text{C}_2\text{H}_4) + G(\text{C}_2\text{H}_2) + G(\text{C}_2\text{H}_5\text{OCH}(\text{CH}_3)\text{C}_2\text{H}_5) \right. \\ &\quad \left. + G(\text{CH}_3(\text{CH}_2)_3\text{OC}_2\text{H}_5) + G(\text{C}_2\text{H}_5\text{OC}_3\text{H}_7) + G(\text{C}_3\text{H}_8) \right\} \\ &= 1.6 \text{ -----IV.13} \end{aligned}$$

The relative probability of C-C bond cleavage, per bond, is given by

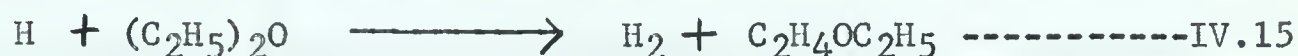
$$\begin{aligned} G(-\text{C-C}) \text{ per bond} &= \frac{1}{2} \left\{ G(\text{CH}_4) + G(\text{C}_2\text{H}_5\text{OCH}(\text{CH}_3)_2) + G(\text{C}_3\text{H}_8) \right\} \\ &= 0.28 \text{ -----IV.14} \end{aligned}$$

The relative ease of bond breakage in an ether molecule is

$$\text{C-O}(G = 1.6) \gg \text{C-H}(G = 0.37) > \text{C-C}(G = 0.28)$$

The C-H bonds rupture more frequently than the C-C bond, though the C-H bonds have higher bond dissociation energies than the latter, which is equal to 85 kcal mole⁻¹, assuming it is the same as $D(\text{C}_2\text{H}_5\text{-CH}_3)$ in propane (87).

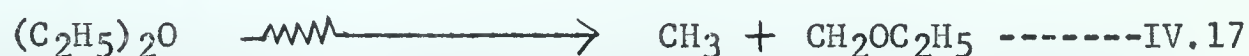
This can be explained, at least in part, by the cage effect. The hydrogen atom is small in size. Therefore, it can diffuse rapidly from its initial liquid cage and undergo abstraction reaction:



The back reaction to form ether (reaction IV.16) probably does not occur appreciably.



In the case of C-C bond cleavage (reaction IV.17), the methyl group formed,

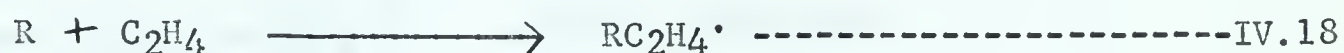


being larger in size than the hydrogen atom, cannot diffuse as readily from the cage. Therefore, an appreciable fraction of the methyl radicals undergoes back reaction to form their parent molecules. The probability of C-O bond cleavage, per bond, is much greater than that of any other type of bonds in the molecule. This is probably because the bond dissociation energy for the C-O bond is the lowest in the molecule, which is estimated at 77 kcal mole⁻¹ (88).

(d) Dose Dependence of Radiolytic Products

Only hydrogen and ethylene yields were observed to vary with dose. The initial hydrogen yield ($G = 3.7$) decreases rapidly to a steady value ($G = 3.4$) at a dose of 5×10^{19} ev/gm. The ethylene yield decreases

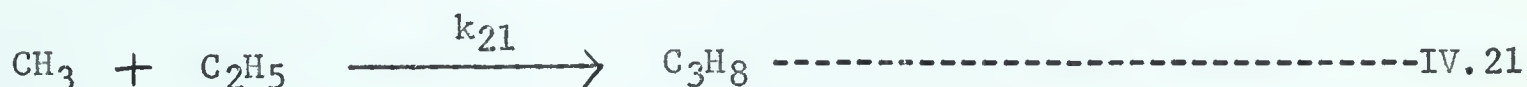
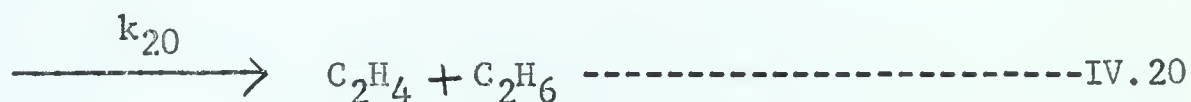
over the entire dose range studied ($0.1 - 4 \times 10^{20}$ ev/gm). Thus $G(H_2)$ and $G(C_2H_4)$ do not decrease at the same rate. The decrease in $G(H_2)$ from 3.7 to 3.4 equals $G(\text{free ions}) = 0.3(89)$. As in ethanol (90), the decrease in the hydrogen yield with increasing dose at low doses seems to be due to the scavenging of solvated electrons by unsaturated products. Ethylene can act as a radical scavenger and, therefore, be destroyed (reaction IV.18).



Since the ethane yield appears to be dose-independent, the radical R in reaction IV.18 is probably not a hydrogen atom.

(e) Methyl and Ethyl Radicals

The combination and disproportionation of methyl and ethyl radicals are represented in the following expressions:



The values of certain ratios of these rate constants have been quite thor-

oughly studied in photolysis and pyrolysis systems in the gas phase. It is assumed that these ratios have the same magnitude in the liquid phase. These values are given below, together with their relations to the G-values.

$$\frac{k_{20}^a}{k_{19}} = \frac{G(\text{IV.20})^b}{G(\text{C}_4\text{H}_{10})} = 0.14\text{---}(92)(93)(91)$$

$$\frac{k_{22}}{k_{21}} = \frac{G(\text{IV.22})}{G(\text{C}_3\text{H}_8)} = 0.06\text{---}(94)(95)$$

$$\frac{k_{21}}{k_{19}^{1/2} k_{23}^{1/2}} = \frac{G(\text{C}_3\text{H}_8)}{G^{1/2}(\text{C}_2\text{H}_6) C^{1/2}(\text{IV.19})} = 2\text{---}(94)(95)$$

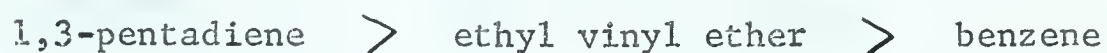
Butane and propane, which are formed from reaction IV.19 and IV.21, respectively, have G-values of 0.053 and 0.078. Thus, $G(\text{IV.21}) \sim 0.007$, $G(\text{IV.22}) \sim 0.005$, and $G(\text{IV.29}) \sim 0.03$. Therefore, reactions IV.20, IV.22 and IV.23 do not contribute appreciably to the overall yields of methane ($G=0.41$), ethylene ($G=1.1$) and ethane ($G=1.27$).

a: This ratio was found to be bigger (0.17-0.20) in the liquid phase (96); it also depends on the kind of solvents used.

b: $G(\text{IV.20})$ is the yield of C_2H_4 or C_2H_6 that results from reaction IV.20. This is not to confuse the C_2H_4 and C_2H_6 that are formed by other reactions.

(B) THE EFFECTS OF ADDITIVES AND THE MECHANISMS OF THE REACTIONS (LIQUID)

Benzene, ethyl vinyl ether and 1,3-pentadiene were the three additives used in the present study. The study of the product yields as functions of additive concentration shows that the effectiveness of the additives as inhibitors varies in the following order:



In Table IV.2, the products are separated into scavengeable and unscavengeable portions by observing the nature of the inhibition curves (Figure III.5 to Figure III.9). It is assumed that the sharp change in the curvature of an inhibition curve is the region where scavenging is complete. The values in Table IV.2 are based on the inhibition curves of 1,3-pentadiene because it is the most efficient inhibitor of the three additives. The H_2 scavengeable and unscavengeable yields can be determined by kinetic analysis (see below).

Probable product-forming reactions will be discussed in the light of the additive studies.

(a) Hydrogen

The hydrogen yield can be decreased by both chemical and physical interactions of the three additives. Enough data had been collected for the ethyl ether-ethyl vinyl ether system for the purpose of kinetic analysis. The scavenging and activation transfer mechanisms will be considered separately. Similar mechanisms have been postulated by Freeman et al (97) for the cyclohexanone-benzene and the cyclohexanone - 2,3-dimethyl-1,3-butadiene systems.

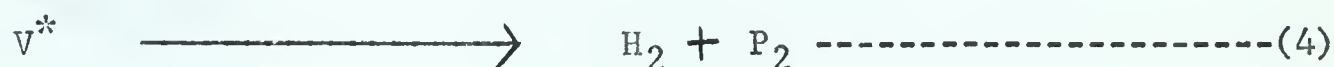
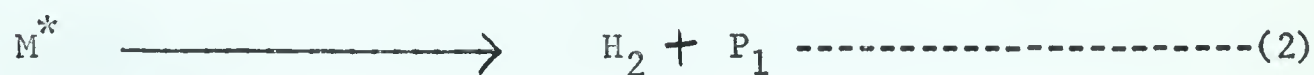
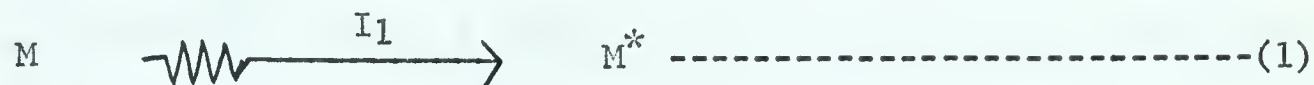
TABLE IV.2Scavengeable and Unscavengeable Yields of Radiolytic Products

(Liquid Phase)

<u>Compound</u>	<u>a</u> <u>G_{sc}</u>	<u>b</u> <u>G_{uns}</u>
Hydrogen	1.4 ± 0.5	2 ± 0.5
2,3-Diethoxybutane	2.55	0.1
Ethanol	1.2	1.0
Ethane	1.1	0.2
Ethylene	1.1	0
s-Butyl ethyl ether	0.64	0.1
Methane	0.31	0.1
Carbon Monoxide	0.0	0.07

a: G_{sc} stands for scavengeable yield.

b: G_{uns} stands for unscavengeable yield.

(1) Mechanism 1 (Activation Transfer)

M and V refer to ether and ethyl vinyl ether respectively. I_1 is the rate of formation of M^* and is related to $G(M^*)$ by

$$G(M^*) = AI_1 \text{-----IV.24}$$

where A is a proportionality constant that includes the dose rate. Reactions (2) and (4) in this mechanism might be two-stepped reactions. Each of P_1 and P_2 may represent more than one product.

The rate of formation of hydrogen, $d'[H_2]/dt$, can be expressed as a function of inhibitor concentration by the following steady-state treatment:

$$\frac{d[M^*]}{dt} = I_1 - k_2[M^*] - k_3[M^*][V] = 0 \text{-----IV.25}$$

$$\frac{d[V^*]}{dt} = k_3[M^*][V] - k_4[V^*] - k_5[V^*] = 0 \text{-----IV.26}$$

$$\frac{d'[H_2]}{dt} = \frac{I_1}{1 + \frac{k_3}{k_2}[V]} \left\{ 1 + \frac{k_3 k_4}{k_2(k_4 + k_5)}[V] \right\} \text{-----IV.27}$$

Rearrangement of equation IV.27 gives

$$\{1 + u[V]\} \rho_1 = 1 + v[V] \quad \text{-----IV.28}$$

$$\text{where } u = \frac{k_3 k_4}{k_2 (k_4 + k_5)}$$

$$\rho_1 = \frac{I_1}{d[H_2]/dt}$$

$$v = k_3/k_2$$

ρ_1 can be calculated from known experimental data as follows: (97)

$$\rho_1 = \frac{I_1}{d[H_2]/dt} = \frac{G(H_2)_{\text{uns}} - G(H_2)_v}{G(H_2)_{\text{obs}} - G''(H_2) - G(H_2)_v} \quad \text{-----IV.29}$$

where $G(H_2)_v$ = radiolytic hydrogen from direct radiolysis of ethyl vinyl ether $= 0.51 \times \epsilon_v$ (ϵ_v = electron fraction of ethyl vinyl ether),

$G''(H_2)$ = hydrogen yield from the scavenging mechanism 2 (Page 98),

$G(H_2)_{\text{obs}}$ = hydrogen yield observed = $G'(H_2) + G''(H_2) + G(H_2)_v$,

$G'(H_2) = Ad'[H_2]/dt$ = hydrogen yield from mechanism 1,

$G(H_2)_{\text{uns}}$ = unscavengeable hydrogen yield.

The denominator of the right hand side of equation IV.29 can be calculated because $G''(H_2)$ can be obtained from mechanism 2 (Page 98). The numerator can be calculated by assuming a value of $G(H_2)_{\text{uns}}$, such that $G(H_2)_{\text{uns}} = G(H_2)_{\text{uns}}^0 \times \epsilon_e$, where ϵ_e is the electron fraction of ether and $G(H_2)_{\text{uns}}^0$ is the unscavengeable hydrogen yield in pure diethyl ether. Thus, with

assumed values of $G(\text{H}_2)_{\text{uns}}^0$, ρ_1 can be calculated. Now, if an arbitrary value is assigned to u , the left hand side of equation IV.28 can be plotted against $[V]$. As defined by equation IV.28, the plot should give a straight line with an intercept of unity and the slope is equal to v . After many trials, $G(\text{H}_2)_{\text{uns}}^0$ is evaluated at 2.0 ± 0.5 . The best plot is shown in Figure IV.1. In Figure IV.1, plots are made with $u = 0.0, 0.2$ and 0.4 which show that $u = 0.2$ gives the best plot and v is equal to 0.43 .

If this mechanism applies, half of the V^* generated in reaction (3) decomposes to form hydrogen ($k_4/(k_4+k_5)=0.5$). The unscavengeable yield of hydrogen is $G = 2.0 \pm 0.5$ and the scavengeable yield is $G = 1.4 \pm 0.5$.

(2) Mechanism 2 (Scavenging)




I_2 is the rate of formation of M^* and is related to $G(\text{M}^*)$ by

$$G(\text{M}^*) = AI_2$$

FIGURE IV.1Kinetic Plot for Activation Transfer Mechanism

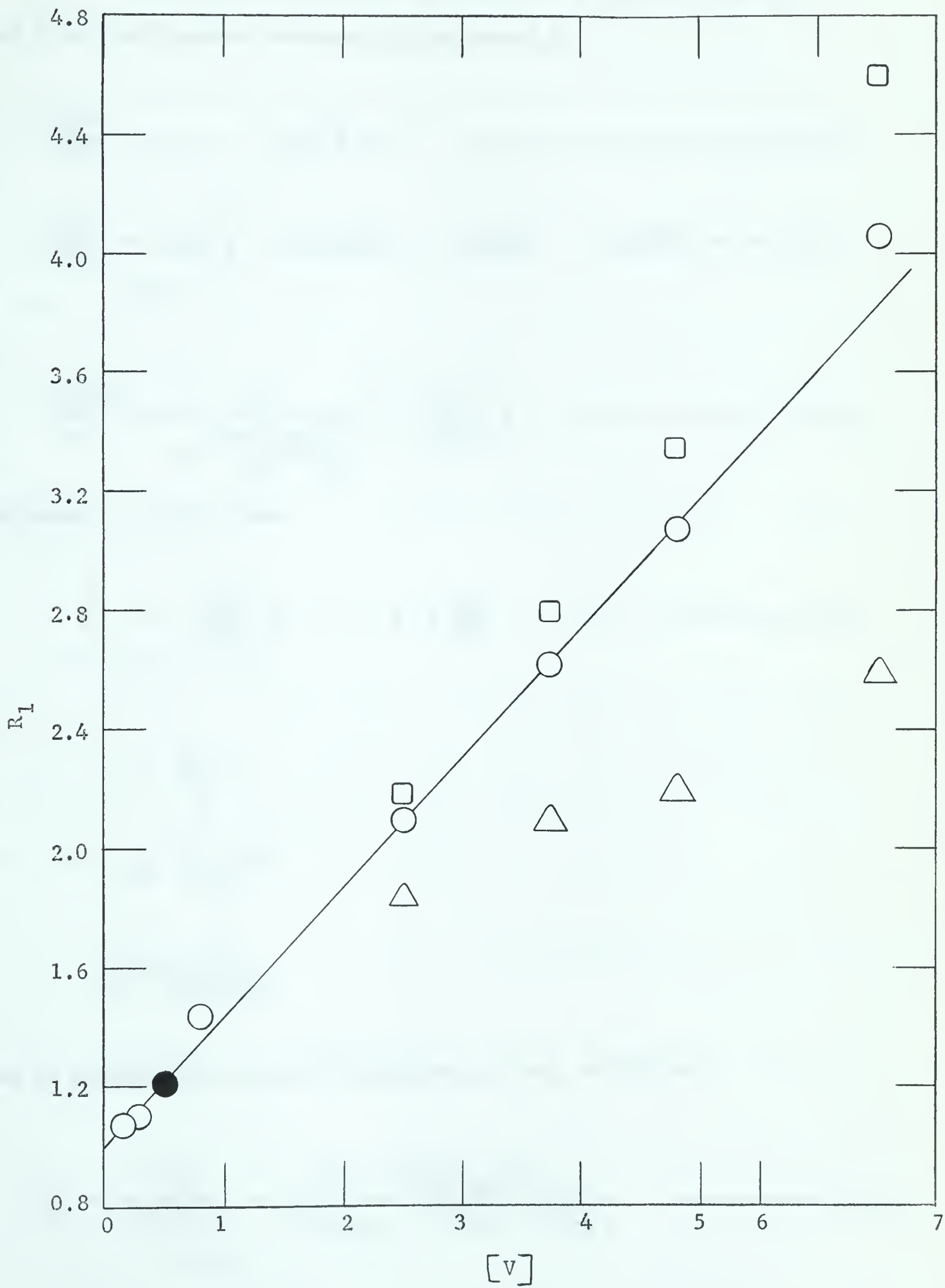
$$R_1 = \left\{ 1 + u[V] \right\} \rho_1$$

All the points are normalized at 

$$\triangle \quad u = 0$$

$$\bigcirc \quad u = 0.2$$

$$\square \quad u = 0.4$$



The rate of formation of hydrogen, $d''[H_2]/dt$, can be derived from steady-state treatment of mechanism 2.

$$\frac{d[M^*]}{dt} = I_2 - k_7[M^*] = 0 \quad \text{-----IV.30}$$

$$\begin{aligned} \frac{d[H]}{dt} &= k_7[M^*] - k_8[H][M] - k_9[H][V] - k_{10}[H][V] \text{-----IV.31} \\ &= 0 \end{aligned}$$

$$\frac{d''[H_2]}{dt} = \frac{I_2}{1 + \frac{k_9 + k_{10}[V]}{k_8[M]}} \left\{ 1 + \frac{k_9[V]}{k_8[M]} \right\} \quad \text{-----IV.32}$$

Rearrangement of IV.32 gives

$$\left\{ 1 + y \frac{[V]}{[M]} \right\} \mathcal{f}_2 = 1 + z \frac{[V]}{[M]} \quad \text{-----IV.33}$$

where

$$y = \frac{k_9}{k_8}$$

$$z = \frac{k_9 + k_{10}}{k_8}$$

$$\mathcal{f}_2 = \frac{I_2}{d''[H_2]/dt}$$

\mathcal{f}_2 can be expressed in terms of experimental data as follows:

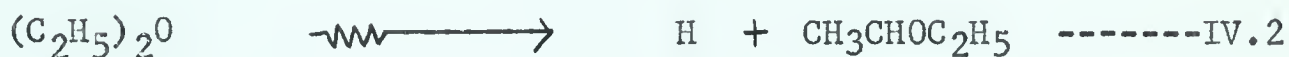
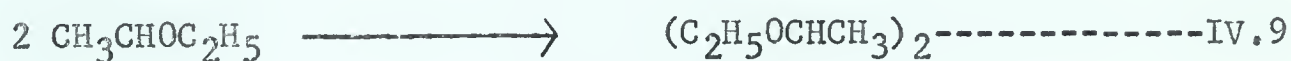
$$\mathcal{f}_2 = \frac{I_2}{d''[H_2]/dt} = \frac{\{3.4 - G(H_2)_{\text{uns}}^0\} \epsilon_e}{G(H_2)_{\text{obs}} - G'(H_2) - G(H_2)_v} \quad \text{-----IV.34}$$

Since $G(\text{H}_2)_{\text{uns}}^0$ and $G'(\text{H}_2)$ can be obtained from the result of the kinetic analysis of mechanism 1, ρ_2 can be calculated from equation IV.39.

Hence, if y is known, the left hand side of equation IV.38 can be plotted against $[V]/[M]$. The plot should be a straight line with an intercept of unity. y is the ratio of the rate of abstraction of a hydrogen atom from ethyl ether to that from ethyl vinyl ether. In the case of ethyl vinyl ether, abstraction reaction would mostly involve a methylenic ($-\text{CH}_2-$) hydrogen. Since there is one methylene group in ethyl vinyl ether and there are two in ethyl ether, the value of y is expected to lie between 0 and 1. The best plot is obtained (Figure IV. 2) when $y=0$, which gives $z=52$. If $y=1$, the slope z is only changed by 3% which is negligible for this purpose.

(b) 2,3-Diethoxybutane

The rapid inhibition of 2,3-diethoxybutane by a small amount ($\epsilon=0.01$) of 1,3-pentadiene indicates that this dimer is formed mostly by radical combination in the bulk solution (reaction IV.9). The α -radicals can be formed according to reactions IV.2 and IV.4.



(c) Ethanol, Ethylene, and Ethane

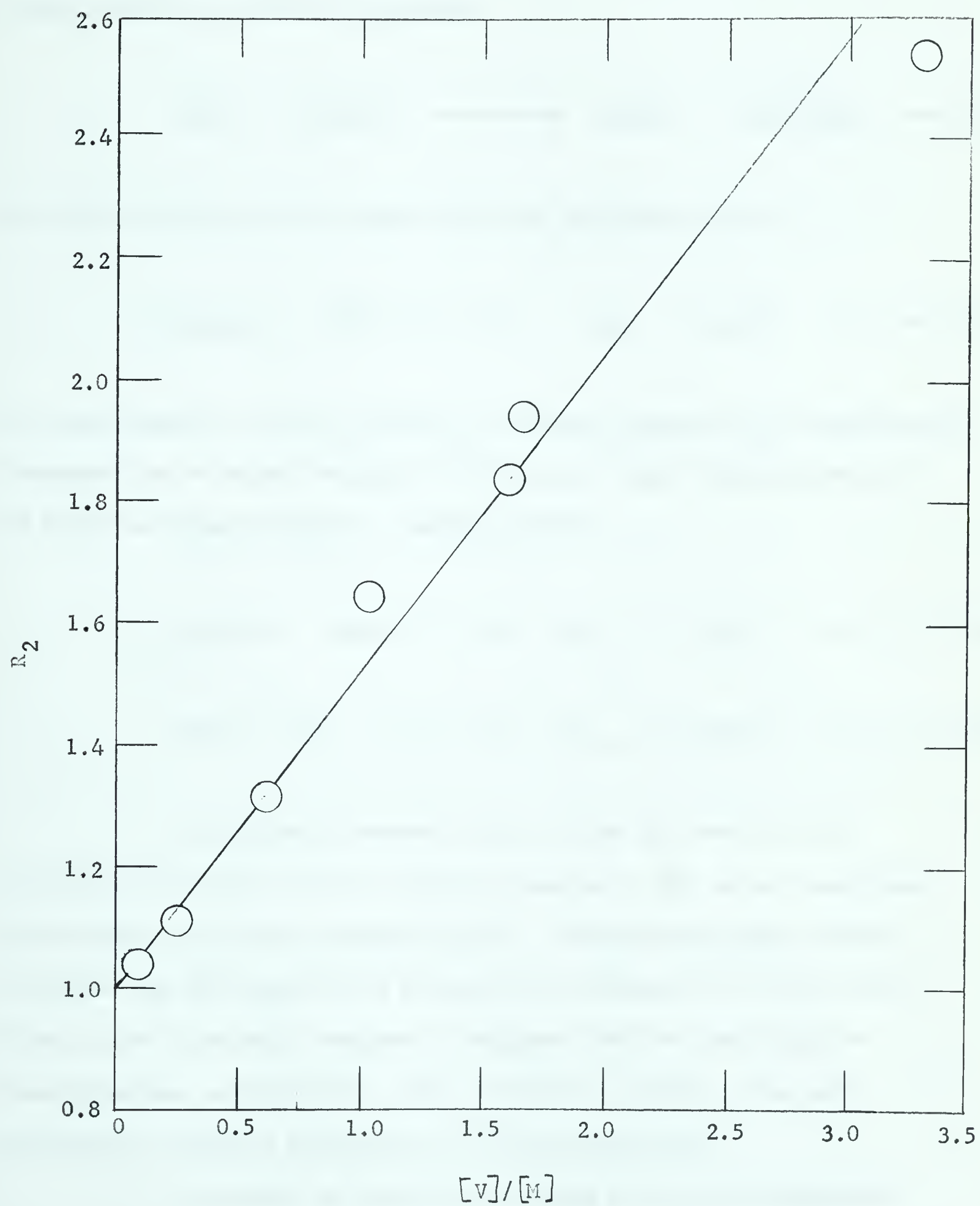
The inhibition of ether radiolysis by 1,3-pentadiene shows

FIGURE IV.2The Kinetic Plot for Scavenging Mechanism

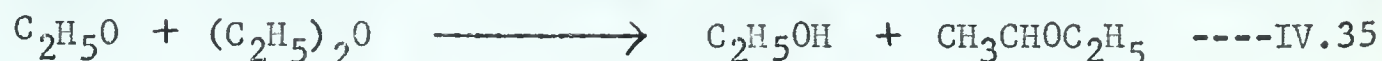
$$R_2 = \left\{ 1 + y \frac{[V]}{[M]} \right\} \rho_2$$

$$y = 0$$

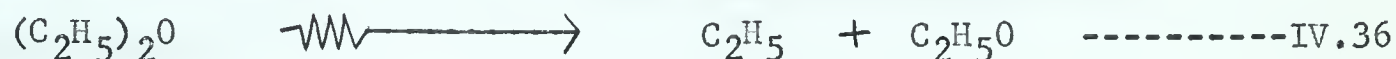
$$z = 52$$



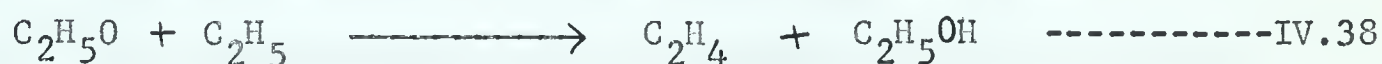
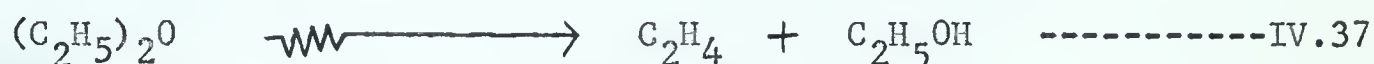
that about half of the ethanol yield is scavengeable ($G_{sc} \sim 1.2$ and $G_{uns} \sim 1.0$). The scavengeable yield probably results from the abstraction reaction of ethoxy radicals in the bulk solution:



The ethoxy radicals can be formed from the following reaction:



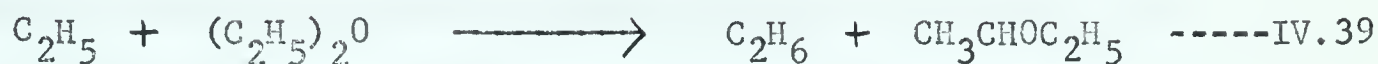
The unscavengeable yield of ethanol is probably formed by the unimolecular decomposition of ether (reaction IV.37), or the cage disproportionation of ethyl and ethoxy radicals (reaction IV.38).



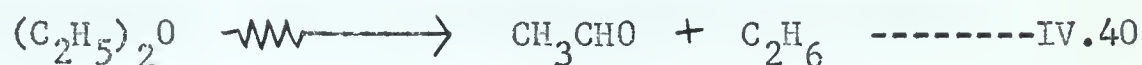
It has been discussed earlier (Page 93) that the disproportionation of two ethyl radicals (reaction IV.20) do not contribute appreciably to the total ethylene yield. Therefore, the most probable reactions for the formation of ethylene are reactions IV. 37 and IV.38. Since there is no sharp decrease of ethylene yield at low inhibitor concentrations, energy and/or charge transfer is probably the main mechanism of ethylene inhibition by the three additives.

The ethane is composed of a large portion of scavengeable yield ($G \sim 1.1$) and a small portion of unscavengeable yield ($G \sim 0.2$).

Therefore, most of the ethane formation involves ethyl radical abstraction in the bulk solution:

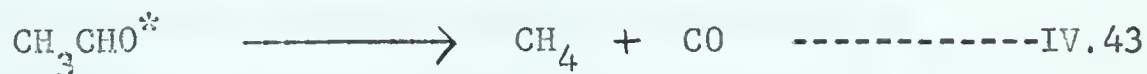


The unscavengeable yield can arise from the unimolecular decomposition of ether (reaction IV.40) and the cage disproportionation of ethyl and ethoxy radicals (reaction IV.41). Ethane and acetaldehyde are formed in both cases.

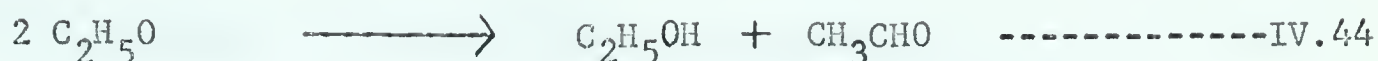


(d) Methane

It is seen, in Table IV.2, that $G(\text{CH}_4)_{\text{uns}} \sim 0.1$ and $G(\text{CH}_4)_{\text{sc}} \sim 0.3$. The scavengeable portion is probably formed by reaction IV.42, while the unscavengeable portion is formed by reaction IV.43, or some similar reaction.



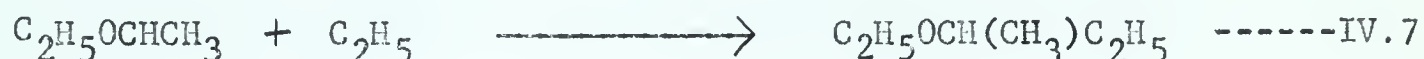
Acetaldehyde can be formed according to reactions IV.40 and IV.41, or by the disproportionation of two ethoxy radicals (reaction IV.44).



The ethoxy radicals are probably consumed by reacting with the substrate and other kinds of radicals before they have a chance to collide with one another. Hence, reaction IV.44 is probably slow compared with reactions IV.40 and IV.41. It follows that most of the acetaldehyde yield ($G=0.18$) is probably formed from reactions IV.40 and IV.41.

(e) s-Butyl Ethyl Ether

Most of the s-butyl ethyl ether ($G=0.64$) is scavengeable by 1,3-pentadiene, which suggests that it is formed mostly by radical reaction (reaction IV.7) in the bulk solution.



(f) Carbon Monoxide

Carbon monoxide formation is not inhibited by any of the additives used. It is probably formed by reaction IV.43, or some similar reaction.

(g) Ethyl Vinyl Ether

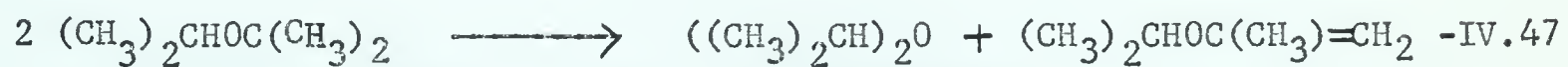
Ethyl vinyl ether can be formed by a unimolecular process (reaction IV.45) or by disproportionation reaction involving an α -radical (reaction IV.46).





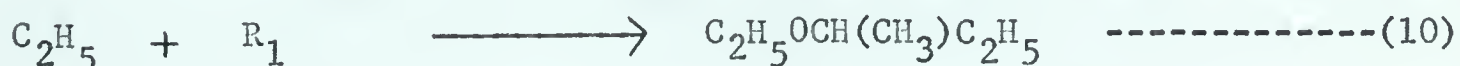
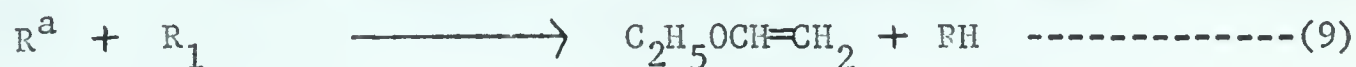
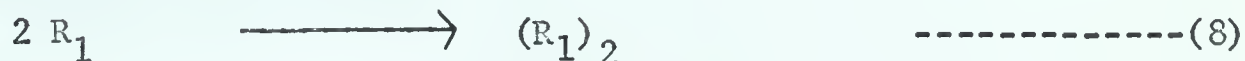
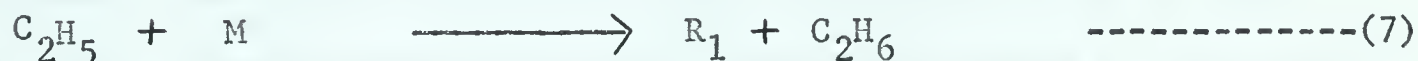
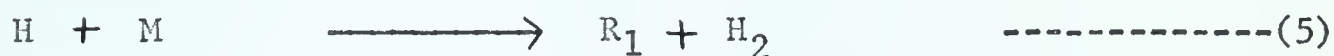
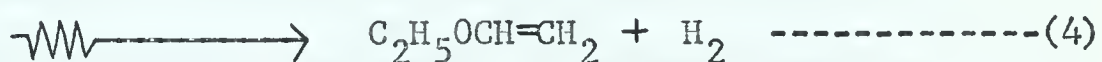
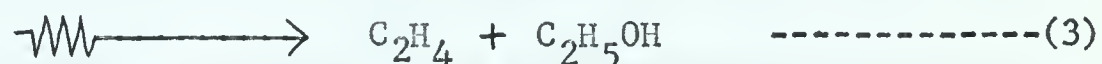
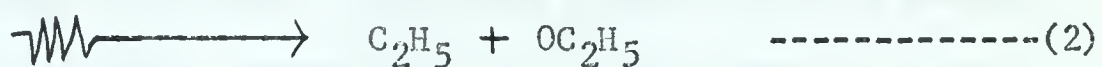
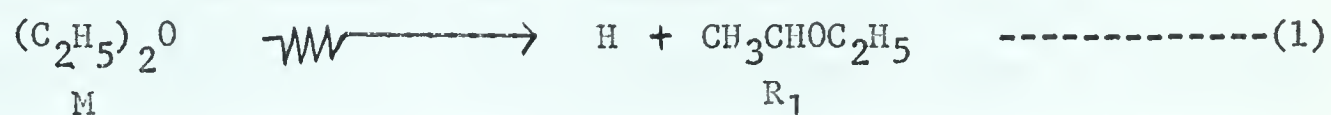
R represents any radical formed. The disproportionation of two 2-isopropoxy-2-propyl radicals has been suggested by Kharasch (98).

α -methyl vinyl i-propyl ether was one of the products of this reaction:



(C) REACTION MECHANISM (LIQUID PHASE)

Investigation of the radiolysis of liquid ethyl ether in the pure phase as well as binary solutions has been carried out and discussed above. In the light of the observations of the experimental data, the following mechanism is postulated, which leads to the formation of the major products ($G > 0.5$).



a: R refers to any radical.

(D) COMPARISON OF GAS PHASE AND LIQUID PHASE RADIOLYSIS(a) Material Balance

The mass balance for the gas phase radiolytic products at a dose of 3.5×10^{20} ev/gm is presented in Table IV.3. Ether is found to decompose with a G-value of 11.6, which is the same as in the liquid phase. The radiolytic products give a formula of $C_4H_{10.33}O_{0.98}$, which shows an excess of $G(H_2) = 1.9$. This poor mass balance might be attributed to polymer formation since the present analytical system can only measure compounds containing up to eight carbon atoms (i.e. the dimers of ether). The decrease in G-value in the case of acetaldehyde and ethyl vinyl ether (see section (c) below) might be the result of polymerisation reactions. An excess of $G(H_2) = 7$ has been observed in the gas phase radiolysis of cyclohexane (99), which is probably the result of polymer formation by ion molecule reactions.

(b) The Fragmentation of Ether Molecules

Although the rate of decomposition of ether is the same in both phases, the product yields are quite different, as it is shown in Table IV.4. These differences can be mainly attributed to the extent of fragmentation reactions IV.48-IV.52.

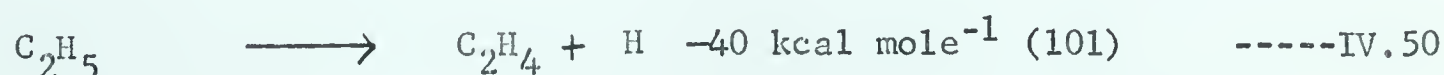
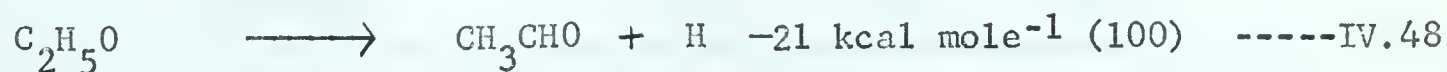


TABLE IV.3Material Balance of Radiolytic Products

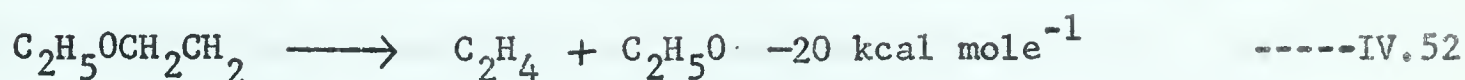
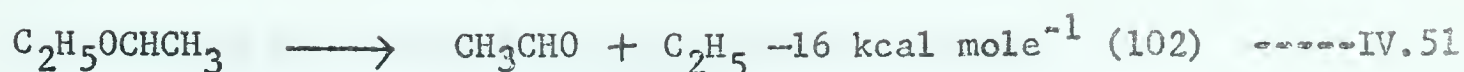
(Gase Phase)

<u>Compound</u>	<u>C</u>	<u>H</u>	<u>O</u>
H_2	0	12.88	0
$(CH_3CHOC_2H_5)_2$	19.04	42.84	4.76
C_2H_4	4.20	8.40	0
CH_3CHO	2.84	5.68	1.42
CH_4	1.26	5.04	0
$C_2H_5OCH(CH_3)_2$	5.00	12.0	1.0
$HCHO$	0.9	1.8	0.9
$C_2H_5OCH(CH_3)C_2H_5$	4.98	11.62	0.83
C_2H_5OH	1.30	3.90	0.65
C_2H_6	0.88	2.64	0
$C_2H_5OCH=CH_2$	1.6	3.2	0.4
CO	0.40	0	0.40
C_2H_2	0.06	0.06	0
C_3H_8	0.43	1.15	0
$CH_2(OC_2H_5)_2$	1.1	2.64	0.44
$CH_3CH(OC_2H_5)_2$	0.54	1.26	0.18
$CH_3OC_2H_5$	0.42	1.12	0.14
Total	45	116.24	11.12

TABLE IV.4Comparision of the G-values of Major Products^a(Dose = 3.5×10^{20} ev/gm)

<u>Compound</u>	<u>G(Liquid Phase)</u>	<u>G(Gas Phase)</u>
Hydrogen	3.4	6.44
2,3-Diethoxybutane	2.63	2.38
Ethanol	2.13	0.65
Ethane	1.27	0.44
Ethylene	0.6	2.10
s-Butyl ethyl ether	0.74	0.83
Methane	0.41	1.26
Acetaldehyde	0.18	1.42
Carbon monoxide	0.07	0.40
Ethyl i-propyl ether	0.07	1.0
Formaldehyde	0	0.9

a: major products are the products having $G > 0.5$ in either liquid or gas phase.



These radicals are probably "hot" radicals.

These decomposition reactions probably occur to a greater extent in the gas phase than in the liquid phase because of less collisional deactivation in the former. These reactions explain the increase of the yields of acetaldehyde, formaldehyde, ethylene, and hydrogen. Reaction IV.49 is partially responsible for the increase of the yield of methyl radicals in the gas phase. The increase of yield of methyl radicals is also attributed to the lack of cage effect in the gas phase. The depletion of ethoxy and ethyl radicals through reactions IV.48, IV.49, and IV.50 probably accounts for the decrease in the yields of ethanol and ethane in the gas phase.

(c) Dose Dependence of Products in the Gas Phase

The yield of acetaldehyde changes from 1.42 at 5×10^{20} ev/gm to 1.0 at 1.87×10^{21} ev/gm. The yield of ethyl vinyl ether is 0.4 at a dose of 1.9×10^{21} ev/gm; it cannot be measured at a lower dose because its chromatographic peak would be entirely covered by the substrate peak. However, when ether was radiolyzed in the presence of 0.3% ethyl vinyl ether, the latter was found to have disappeared by 0.044% at 5.0×10^{20} ev/gm. Therefore, it seems that ethyl vinyl ether would have a higher G-value than 0.4 at a lower dose. These decreases in yields as the dose is increased are probably due to secondary reactions.

The other products are found to be independent of dose at 1, 2, and 3×10^{20} ev/gm (Table III.6).

(d) Combination and Abstraction Reactions of Radicals

The values of the ratios $G(\text{s-butyl ethyl ether})/G(\text{ethane})$ and $G(\text{ethyl i-propyl ether})/G(\text{methane})$ are presented in Table IV.5. It is observed that the ratio $G(\text{combination})/G(\text{abstraction})$, or R_c/R_a , is larger in the gas phase than in the liquid phase. This can be explained in the following way.

In the liquid phase, two particles (molecules or/and radicals) are considered to encounter each other when one is in the wall of the "cage" of the other. This configuration will endure for a certain time before one of the particles diffuses away. During that interval, the two particles can collide many times with each other. In other words, repeated collisions between the same two particles are very favorable in the liquid phase due to the cage effect(103). Since abstraction reactions usually have low collision efficiency ($\sim 10^{-9}$ for the abstraction reaction $\text{CH}_3 + (\text{i-C}_3\text{H}_7)_2\text{O} \longrightarrow \text{CH}_4 + \text{C}_3\text{H}_7\text{OC}_3\text{H}_6$) (91), repeated collisions tend to enhance the rates of abstraction reactions in the liquid phase. Radical combination reactions are not benefited by repeated collisions because these reactions probably occur at the first collision.

Due to more rapid diffusion in the gas phase, fresh collisions are preferred to repeated collisions. Therefore, abstraction reactions are less favorable, and combination reactions more favorable in the gas phase than in the liquid phase.

TABLE IV.5The Ratio of G(Combination)/G(Abstraction) of Radicals

<u>Ratio</u>	<u>Liquid Phase</u>	<u>Gase Phase</u>
$\frac{G(C_2H_5OCH(CH_3)C_2H_5)}{G(C_2H_6)}$	0.58	1.9
$\frac{G(C_2H_5OCH(CH_3)_2)}{G(CH_4)}$	0,17	0.79

(E) PROTECTION BY 1,3-PENTADIENE (GAS PHASE)

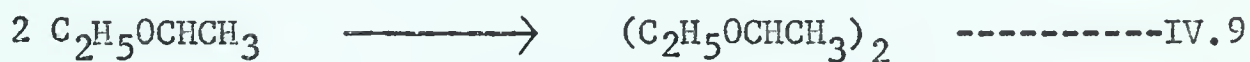
The observed products in the gas phase radiolysis are separated into scavengeable and unscavengeable portions according to whether or not they are inhibited by 1,3-pentadiene (Table IV.6). It is assumed that the sharp change in the curvature of an inhibition curve (Figure III.10 and 11) is the region where scavenging is complete.

(a) Hydrogen

A large portion of the hydrogen yield is inhibited by 1,3-pentadiene. The inhibition curve is about the same as in the liquid phase since the ratio $G(H_2)$ in the liquid phase to $G(H_2)$ in the gas phase is ~ 0.6 when the electron fractions of 1,3-pentadiene are 0, 0.1, and 0.2.

(b) 2,3-Diethoxybutane

Most of the 2,3-diethoxybutane is scavengeable, such as it is in the liquid phase. The reaction mechanism (reaction IV.9) is probably the same in both phases.

(c) Ethylene, Ethanol, and Ethane

The ethylene yield ($G=2.1$) is only slightly affected by 1,3-pentadiene (Figure III.11), indicating that its formation is mainly through unimolecular decompositions such as reactions IV.37, IV.50, and IV.52.

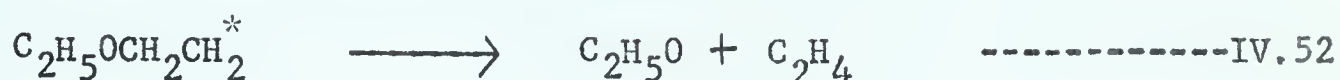
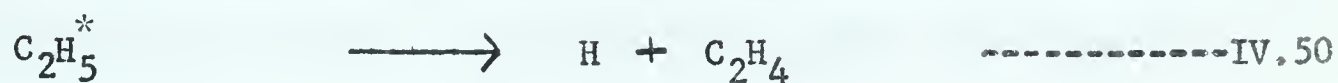
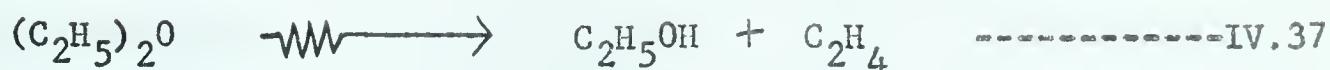
TABLE IV.6Scavengeable and Unscavengeable Yields of Radiolytic Products

(Gas Phase)

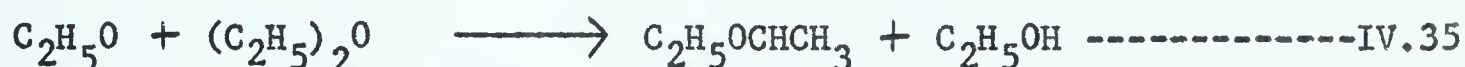
<u>Compound</u>	<u>G_{sc}^a</u>	<u>G_{uns}^b</u>
Hydrogen	4.4	2
2,3-Diethoxybutane	2.28	<0.1
Ethylene	0	2.1
Methane	0.9	0.36
Ethanol	0.6	<0.05
Ethane	0.34	0.1
Carbon monoxide	0	0.4

a: G_{sc} stands for scavengeable yield.

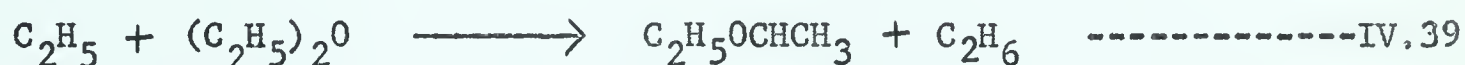
b: G_{uns} stands for unscavengeable yield.



Reaction IV.37 is unlikely since most of the ethanol yield (0.65) is scavengeable. Ethanol is probably formed by hydrogen abstraction reaction by ethoxy radicals (reaction IV.35).

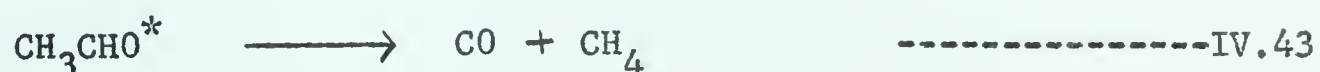


Ethane ($G=0.44$) has a scavengeable yield of 0.34. Ethane is probably formed from reactions IV.39 and IV.40, the former gives the major contribution.



(d) Methane

Methane has a scavengeable yield of ~ 0.9 and an unscavengeable yield of ~ 0.4 . Therefore, most of the methane is probably formed by reaction IV.42, and a lesser portion of it is formed by reaction IV.43.

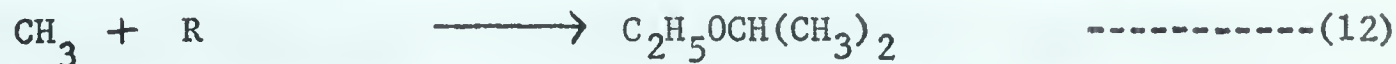
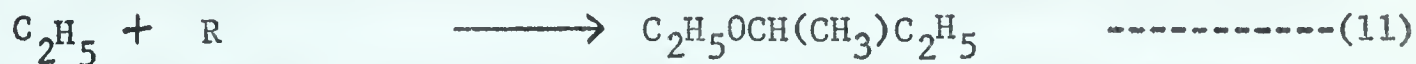
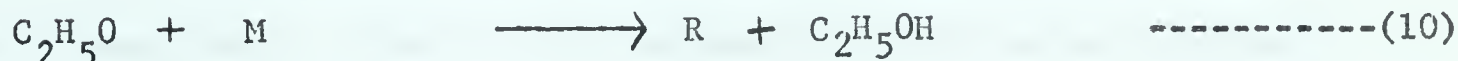
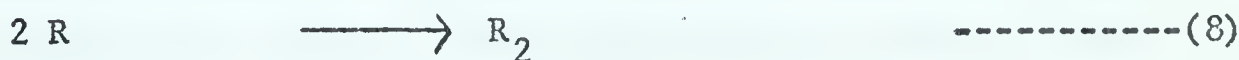
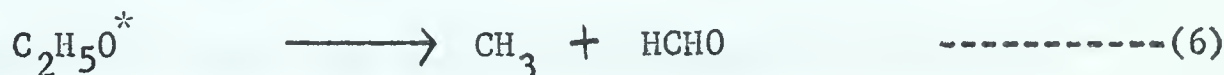
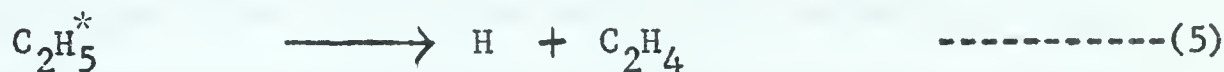
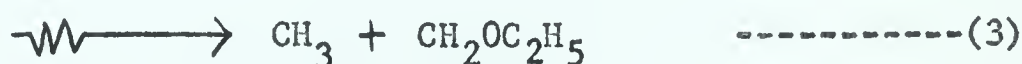
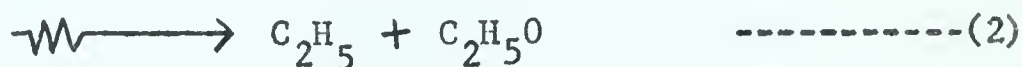
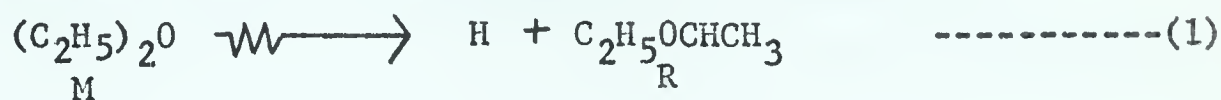


(e) Carbon Monoxide

Carbon monoxide is only slightly affected by 1,3-pentadiene. This suggests that it is formed, as in the liquid phase, from reaction IV.43, or some similar unimolecular reaction.

(F) REACTION MECHANISM IN THE GAS PHASE

In view of the observations made on the gas phase radiolysis, the following mechanism is postulated for the formation of products having $G > 0.5$. As it was mentioned earlier, the main difference between the gas phase and liquid phase radiolysis is attributed to the fragmentation reactions IV.48-IV.52, as well as to the cage effect.



(G) THE LIQUID PHASE RADIOLYSIS OF DEUTERATED ETHERS

It is very unfortunate that the deuterated ethers contain a considerable amount of impurities (Table II.1). Many of the impurities, which are present in small amount ($< 0.1\%$) have not been identified. Acetone and isotopic impurities are present in large amount and their effects on the hydrogen yield are corrected for. All the data, corrected or uncorrected, should be interpreted with a degree of reservation.

(a) Hydrogen(1) Corrections

The hydrogen yield corrections for the presence of acetone and isotopic impurities are carried out in the following manner.

The liquid phase radiolysis of a 0.7% solution, by weight, of acetone in light ether shows that $G(H_2)$ is decreased by 11.8% as compared with the pure ether radiolysis. Now, it is assumed that $G(Hyd)$, which is the total hydrogen yield, is decreased by the same amount, i.e., 11.8%, in all the deuterated ethers, in the liquid phase as well as the gas phase. The corrected values are presented in Table IV.7.

The corrections for the isotopic impurities are made with two assumptions. Firstly, the deuterated ethers do not interact upon mixing, i.e. $G(Hyd)$ for one ether component is directly proportional to its electron fraction. Secondly, the isotopic impurities are one or more of the four ether entities: ether- d_0 , ether- α - d_4 , ether- β - d_6 and ether- d_{10} . For example, if ether- β - d_6 has ether- α - d_4 as an impurity which has an electron fraction of x , then the corrected $G(Hyd)$ can be obtained from the following expression:

TABLE IV.7Hydrogen Yield in the Radiolysis of Deuterated Ethers

(Pure Liquid Phase)

<u>Ether</u>	G(Hyd) ^a uncorrected	G(Hyd) ^b corrected for acetone	G(Hyd) corrected for acetone and <u>isotopic impurities</u>
(C ₂ H ₅) ₂ O	3.43	3.0	3.0
(CH ₃ CD ₂) ₂ O	2.14	2.14	2.12
(CD ₃ CH ₂) ₂ O	3.04	2.68	2.9
(C ₂ D ₅) ₂ O	1.70	1.62	1.52

a: $G(\text{Hyd}) = G(\text{H}_2) + G(\text{HD}) + G(\text{D}_2)$

b: The values in this column are the values of G(Hyd) for the ethers at 0.7% acetone concentration. The first two values (3.0 and 2.14) are experimental values. The last two values (2.68 and 1.62) are obtained as described on the previous page.

$$G(\text{Hyd})_{\text{corr.}} = \left\{ G(\text{Hyd})_{\text{d}_6} - xG(\text{Hyd})_{\text{d}_4} \right\} / (1 - x)$$

where $G(\text{Hyd})_{\text{corr}}$ = corrected value of $G(\text{Hyd})$,

$G(\text{Hyd})_{\text{d}_6} = 2.68$, the $G(\text{Hyd})$ in ether- β - d_6 after correcting for acetone,

$G(\text{Hyd})_{\text{d}_4} = 2.14$, the $G(\text{Hyd})$ in ether- α - d_4 after correcting for acetone.

The values of $G(\text{Hyd})_{\text{corr}}$ for all the ethers investigated are presented in Table IV.7.

(2) Analysis of the Data

(i) Specificity of Reaction of C-H Bonds

The values of $G(\text{Hyd})$ for the liquid and gas phase radiolysis of pure ethers are presented in Table IV.7, together with the corrected values. If there were no specificity of the C-H bonds, the values of $G(\text{Hyd})$ should decrease in proportion to the deuterium contents of various ethers. It is seen from Table IV.7 that $G(\text{Hyd})$, both corrected and uncorrected, is considerably higher for ether- β - d_6 than ether- α - d_4 , even though the former contains more deuterium. This clearly demonstrates that β -deuterium substitution has a small effect on the hydrogen yield, or, in other words, the α -C-H bond is a more reactive site than the β -C-H bond. This specificity is also reflected in the percent deuterium in the radiolytic hydrogen (Table IV.8). The value of %D is higher for ether- α - d_4 than ether- β - d_6 , despite the smaller deuterium content of the former molecule.

(ii) Isotope Effect

TABLE IV.8

Isotopic Composition in the Radiolytic Hydrogen

(Liquid Phase)

A. Uninhibited Systems

	<u>% H₂</u>	<u>% HD</u>	<u>% D₂</u>	<u>% D^a</u>
(D ₂ H ₅) ₂ O	100	0	0	0
(CH ₃ CD ₂) ₂ O	25.8	50	24.2	65.5
(CD ₃ CH ₂) ₂ O	75	22.5	2.5	18.9
(C ₂ D ₅) ₂ O	1.7	5.3	93	98.3

B. Inhibited Systems ($\epsilon_p^b = 0.17$)

	<u>% H₂</u>	<u>% HD</u>	<u>% D₂</u>	<u>% D</u>
(C ₂ H ₅) ₂ O	100	0	0	0
(CH ₃ CD ₂) ₂ O	41	43	16	47.7
(CD ₃ CH ₂) ₂ O	69.5	25.8	4.7	20.2
(C ₂ D ₅) ₂ O	13.8	29.4	57	84

$$a: \quad \% D = \frac{2G(D_2) + G(HD)}{2G(D_2) + G(HD) + 2G(H_2)} \times 100$$

$$b: \quad \epsilon_p = \text{electron fraction of 1,3-pentadiene.}$$

The γ and π factors, the ratio γ/π (Page 15), and the overall isotope effect are presented in Table IV.9. The γ and π factors are nonlinear functions of the deuterium contents of the ether molecules. This again demonstrates the specificity of the α -C-H bond.

In radiolysis, molecules usually absorb energy that far exceeds the bond dissociation energies of the molecules. Therefore, the primary bond-breaking processes are probably non-specific. It follows that if the primary processes are mostly responsible for the formation of molecular hydrogen, then, the ratios γ/π are expected to be about the same as the overall isotope effect. The fact that the ratios γ/π (0.69 and 9.4) differ considerably from each other as well as from the overall isotope effect (2.0) indicates that a secondary reaction is very important for hydrogen formation. This is probably the abstraction by hydrogen atoms from ether molecules .

(iii) Inhibition by 1,3-Pentadiene ($\epsilon = 0.17$)

Investigations were made for the radiolysis of solutions of 1,3-pentadiene ($\epsilon = 0.17$) in the various deuterated ethers. The isotopic compositions of the radiolytic hydrogen are given in Table IV.8. Similar conclusions pertaining to the specificity of the α -C-H bond can be drawn from these data.

(b) Methane and Carbon Monoxide

The percent isotopic compositions of the radiolytic methanes from the deuterated ethers are given in Table IV.10.

(1) Uninhibited Systems

TABLE IV.9

	<u>Isotope Effect</u>			<u>Overall Isotope Effect</u>
	<u>γ^a</u>	<u>π^b</u>	<u>γ/π</u>	
$(C_2H_5)_2O$	1	-	-	
$(CH_3CD_2)_2O$	0.53	0.774	0.69	
$(CD_3CH_2)_2O$	1.93	0.21	9.4	
$(C_2D_5)_2O$	-	0.5	-	2

a: $\gamma = \frac{\text{H/C-H bond in deuterated Ether}}{\text{H/C-H bond in } (C_2H_5)_2O}$

b: $\pi = \frac{\text{D/C-D bond in deuterated Ether}}{\text{H/C-H bond in } (C_2H_5)_2O}$

TABLE IV.10

Isotopic Composition of Methane

A. Pure

	<u>% CH₄</u>	<u>% CDH₃</u>	<u>% CD₂H₂</u>	<u>% CD₃H</u>	<u>% CD₄</u>
(C ₂ H ₅) ₂ O	100%	0	0	0	0
(CH ₃ CD ₂) ₂ O	50.5	46.6	2.9	0	0
(CD ₃ CH ₂) ₂ O	17.2	9.9	8.3	60	4.6
(C ₂ D ₅) ₂ O	3.4	3.8	0	10.8	82

B. Inhibited (20% 1,3-pentadiene)

	<u>% CH₄</u>	<u>% CDC₃</u>	<u>% CD₂H₂</u>	<u>% CD₃H</u>	<u>% CD₄</u>
(C ₂ H ₅) ₂ O	100	0	0	0	0
(CH ₃ CD ₂) ₂ O	50.8	44.8	4.4	0	0
(CD ₃ CH ₂) ₂ O	14.3	11.1	9.5	57.2	7.9
(C ₂ D ₅) ₂ O	13	0	0	32	55

The value of the ratio $G(\text{CH}_4)/G(\text{CH}_3\text{D})$ for the radiolysis of ether- $\alpha\text{-d}_4$ is ~ 0.5 , whereas the value of $G(\text{CD}_3\text{H})/G(\text{CD}_4)$ for the radiolysis of ether- $\beta\text{-d}_6$ is 13. This indicates that the $\alpha\text{-C-H}$ bond is a more reactive site for hydrogen abstraction by a methyl group.

(2) Inhibited Systems

The distribution of isotopic composition of methane was similar to that in the uninhibited systems. This suggests that at least a portion of the completely inhibited yield of methane arises from radical abstraction reactions. The unscavengeable methyl radicals are probably hot radicals.

The values of $G(\text{total methane})$ and $G(\text{CO})$ (Table III.8) decrease initially and then increase as the deuterium content of ether is increased. It is uncertain whether this is real or it is a complication by impurities.

(c) Ethylene

In the radiolysis of ether- $\alpha\text{-d}_4$, there is 72% of ethylene- d_2 (Table III.10), which suggests that ethylene formation involves mostly $\beta\text{-C-H}$ cleavage:



The 28% of ethylene- d_1 indicates that $\alpha\text{-C-H}$ cleavage also contributes to the formation of ethylene.



This reaction might involve the formation and the subsequent rearrangement of an ethylidene radical.

(d) Ethane

Ethane- d_3 and - d_4 were obtained in the radiolysis of ethyl ether- $\beta\text{-d}_6$. Ethane- d_3 is about 60% of the total ethane yield (Page 80). It shows that ethane formation involves both $\alpha\text{-C-H}$ and $\beta\text{-C-H}$ cleavages.

(H) THE GAS PHASE RADIOLYSIS OF DEUTERATED ETHERS

The results of the radiolysis of the deuterated ethers in the gas phase are similar to that obtained in the liquid phase (Table III.9, III.10, IV.11, IV.12, and IV.13)

TABLE IV.11

Isotopic Composition in the Radiolytic Hydrogen of Deuterated Ethers

(Gas Phase)

A. Uninhibited Systems

	<u>% (H₂)</u>	<u>% (HD)</u>	<u>% D₂</u>	<u>% D^a</u>
(C ₂ H ₅) ₂ O	100	0	0	0
(CH ₃ CD ₂) ₂ O	32.1	50	18.9	57.8
(CD ₃ CH ₂) ₂ O	73.3	24.4	2.3	16.6
(C ₂ D ₅) ₂ O	3.1	2.4	94.5	97

B. Inhibited Systems (ε_p = 0.17)

	<u>% (H₂)</u>	<u>% (HD)</u>	<u>% D₂</u>	<u>% D^a</u>
(C ₂ H ₅) ₂ O	100	0	0	0
(CH ₃ CD ₂) ₂ O	47	42	11	40.5
(CD ₃ CH ₂) ₂ O	71.4	22.9	5.7	19.4
(C ₂ D ₅) ₂ O	24.6	35.6	39.8	70.1

$$a: \quad \% D = \frac{G(HD) + 2G(D_2)}{2G(H_2) + G(HD) + 2G(D_2)} \times 100$$

TABLE IV.12Isotope Effects in the Gas Phase Radiolysis of Deuterated Ethers

	<u>γ</u>	<u>π</u>	<u>γ/π</u>	<u>Overall Isotope Effect</u>
$(C_{2H_5})_2O$	1	-	-	-
$(CH_3CD_2)_2O$	0.55	0.65	0.85	-
$(CD_3CH_2)_2O$	2.0	0.23	9.1	-
$(C_2D_5)_2O$	-	0.5	-	2

TABLE IV.13

Isotopic Composition of Radiolytic Methane in Deuterated Ethers

(Gas Phase)

A. Pure Gas Phase

	<u>% CH₄</u>	<u>% CDH₃</u>	<u>% CD₂H₂</u>	<u>% CD₃H</u>	<u>% CD₄</u>
(C ₂ H ₅) ₂ O	100	0	0	0	0
(CH ₃ CD ₂) ₂ O	51	42.8	6.2	0	0
(CD ₃ CH ₂) ₂ O	13.8	10.0	8.6	63.2	4.4
(C ₂ D ₅) ₂ O	7.3	5.7	0	12	75

B. Additive = 20% 1,3-pentadiene

	<u>% CH₄</u>	<u>% CDH₃</u>	<u>% CD₂H₂</u>	<u>% CD₃H</u>	<u>% CD₄</u>
(C ₂ H ₅) ₂ O	100	0	0	0	0
(CH ₃ CD ₂) ₂ O	37	54.3	7	1.7	0
(CD ₃ CH ₂) ₂ O	19.2	9.6	9.1	57.6	4.5
(C ₂ D ₅) ₂ O	7.7	0	0	68.5	23.8

(I) COMPARISON OF THE γ -RADIOLYSIS OF ETHER, ETHANOL AND WATER(a) Liquid Phase(1) G(disappearance)

It is seen in Table IV.14 that the values of G(disappearance) are in the following order:

$$G_{-(C_2H_5)_2O} > G_{-C_2H_5OH} > G_{-H_2O}$$

This trend and its magnitude can be explained by comparing the major reaction mechanisms in the three systems.

(i) Water

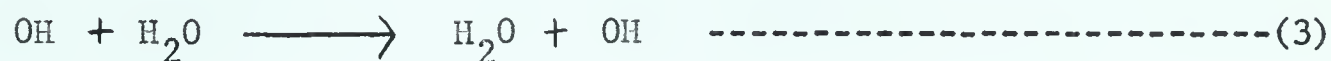
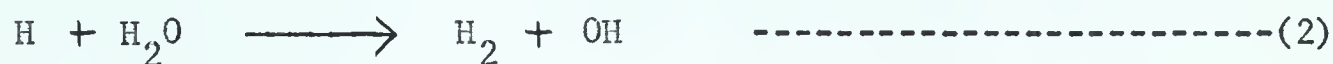
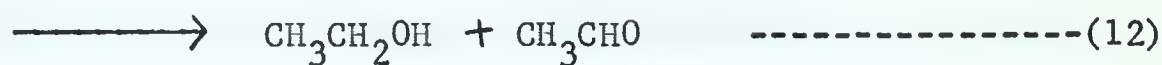
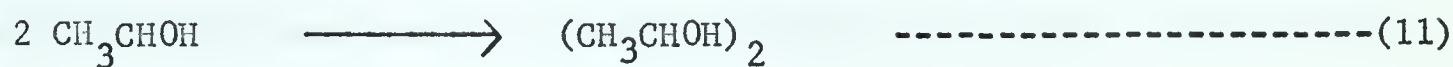
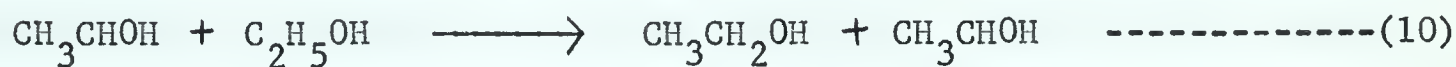
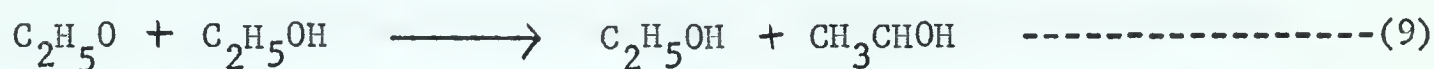
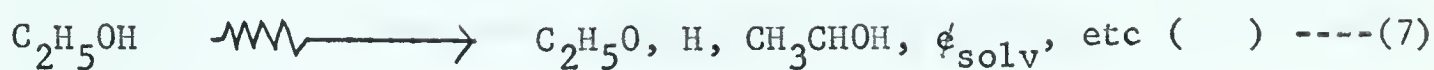
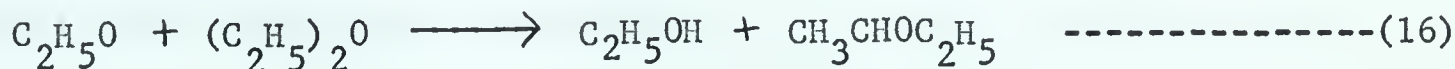
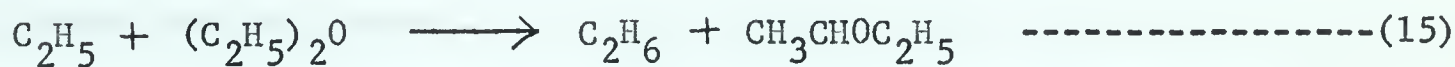
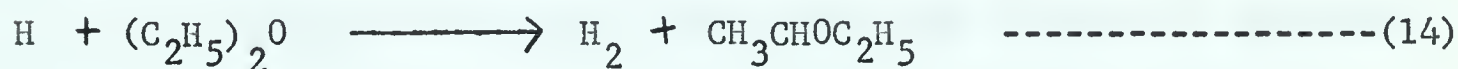
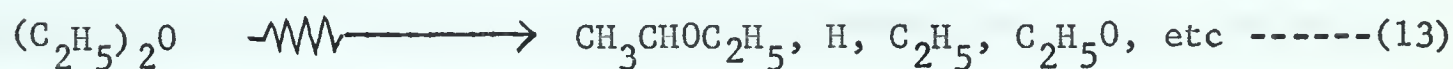
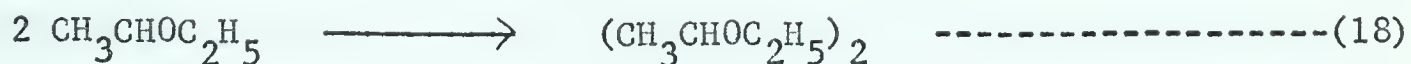


TABLE IV.14Comparison of the γ -Radiolysis of Ether, Ethanol, and Water

	<u>Ether</u>	<u>Ethanol</u>	<u>Water</u>	<u>Reference</u>
G(Disappearance) (liquid phase)	11.3 (25°C)	7.5 (25°C)	3.64 (25°C)	(90) (104)
G(Disappearance) (gas phase)	11.6 (25°)	13.9 (105°C)	11.7 (115°C)	(105) (106)
G(Free ion)	0.3	1.0	2.85 (pH=7)	(89) (107) (108)
Dielectric Constant (25°C)	4.3	24.3	78.5	(109)
Ionization potential (ev)	9.53	10.5	13.2	(70) (110) (111)
Bond dissociation energy (kcal mole ⁻¹)	D(C ₂ H ₅ OCH(CH ₃)-H) = 94	D(HOCH(CH ₃)-H) = 90	D(HO-H) = 118	(81) (112) (37)

(ii) Ethanol(iii) Ether

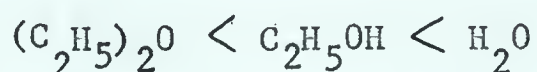


In the radiolysis of water, reaction (2) is unlikely because of its endothermicity ($\sim 14 \text{ kcal mole}^{-1}$). Reaction (3) does not lead to any net disappearance of the substrate. Reaction (6) reduces the net decomposition by the regeneration of water molecule. Therefore, it is expected that one activated species formed will result approximately in the disappearance of one water molecule.

In the radiolysis of ethanol, reactions (7) (8) (9) and (10) predict the disappearance of two ethanol molecules with the formation of one activated species. This rate of disappearance will be decreased by reaction (12) by which the substrate is regenerated. Therefore, it is expected that there are between one to two ethanol molecules destroyed per activated species formed.

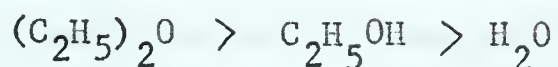
In the radiolysis of ether, the same channel of reasoning predicts that there are between one to three ether molecules destroyed per activated species formed.

It is observed in Table IV. 14 that the ionization potentials are in the following order:



Since the number of activated species formed depends, to some extent, on the ionization potentials of various molecules, the number of activated species

formed should be



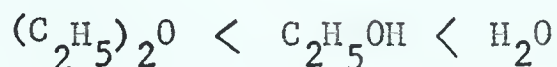
Taking the value of $G_{-\text{H}_2\text{O}}$ as unity, the values of $G(\text{disappearance})$ will give the following ratio:

3.1 in ether : 2.1 in ethanol : 1 in water

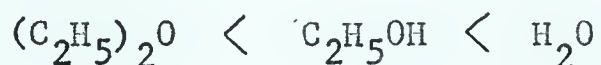
which is in agreement with the above consideration.

(2) Free Ions

The values of $G(\text{Free ions})$, as shown in Table IV.14 are in the following order:



and the dielectric constants for the three compounds are



The higher the dielectric constant is, the less is the electrostatic attraction between an electron and its parent ion at a given separation distance. This makes it more probable for the electron to escape the field of the parent ion and thus becomes a "free ion".

(3) The Change in the Rate of Decomposition by the Addition of Acids

In Table IV.15, it is observed that the values of $G(H_2)$ in ethanol (114), water (116), and cyclohexane (113) increase by about one G unit when a small amount of inorganic acid is added to the systems. However, ethanol radiolysis is not affected by the presence of organic acids (115). The effects of acids on the ether system have not been investigated. However, the acids will probably affect the ether radiolysis similarly, since most chemical and physical properties of ether lie between those of ethanol and a hydrocarbon(e.g. cyclohexane). The mechanism that leads to these effects is not yet known.

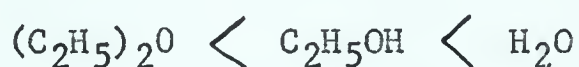
TABLE IV.15The Effects of Acids on the Liquid Radiolysis of Water, Ethanol, and Cyclohexane

<u>Compound</u>	<u>Acid and Concentration</u>	<u>G(H₂)</u>	<u>Reference</u>
Cyclohexane	0.00	4.85	(113)
Cyclohexane	0.20 M HCl	6.05	(113)
Ethanol	0.00	4.9	(50)
Ethanol	0.20 M H ₂ SO ₄	5.9	(114)
Ethanol	0.10 M CH ₃ COOH	4.9	(115)
Water	0.00	2.8 (G _H)	(116)
Water	0.2 N H ₂ SO ₄	3.7 (G _H)	(104)

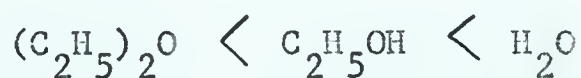
(b) Gas Phase

The values of $G(\text{disappearance})$ of the three compounds in the gas phase are presented in Table IV.14. It is seen that the value of $G(\text{disappearance})$ in the case of ether is unaffected by the change of phase from liquid to vapor, whereas it is doubled in the case of ethanol and tripled in the case of water. The two- and three-fold increases in the respective systems may be due partially to the increase of temperature. However, the radiolysis of methanol vapor at room temperature also showed a two-fold increase (117) over the liquid phase radiolysis. Therefore, it seems that the increase is associated with the particular system rather than the change of temperature.

It is expected that the relative probabilities of cluster formation are



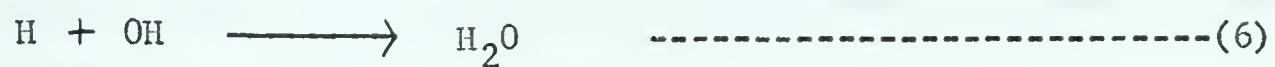
because their dipole moments are



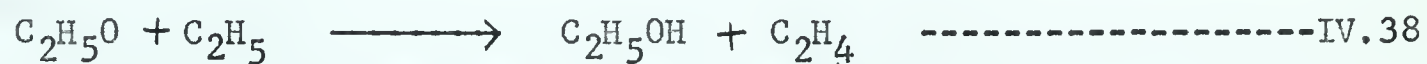
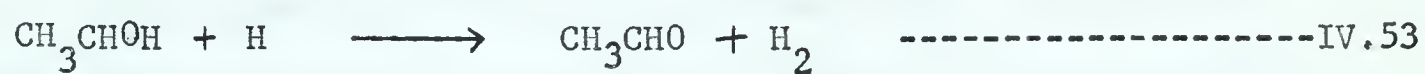
If the neutralization of a cluster leads to the decomposition of several molecules, then cluster formation might be the cause of the observed trend.

The observed trend may also be due to the presence of back reactions in the cage in the liquid phase and the absence of it in the gas phase. The net decomposition of water in the liquid phase is reduced by

reaction (6) in the cage. .



In ethanol and ether, the radicals that are formed in the cage may disproportionate rather than combine with one another:



Hence phase change does not affect ether and ethanol as much as water.

(J) CONCLUDING REMARKS

The present work is the first detailed investigation of the radiolysis of ethyl ether, which includes the measurements of most of the radiolytic products.

Product analyses and studies of deuterated ethers show that α - C-H cleavage is preferred to β - C-H cleavage both in the primary act and in secondary abstraction reactions.

The formation of molecular hydrogen might involve three activated species: free ions, scavengeable H-atoms, and unscavengeable precursors.

Part of the ethylene formed probably involves the formation and rearrangement of ethylidene radicals.

Benzene seems to inhibit product yields mostly by activation transfer mechanism, whereas ethyl vinyl ether and 1,3-pentadiene act as radical scavengers as well.

The change of phase from liquid to vapor does not alter the rate of the radiolytic decomposition of ether; it only leads to fragmentation into smaller entities in the latter.

An interesting comparison of the similarities and differences of the radiolysis of ether, ethanol, and water has been made.

The reaction mechanisms proposed for the radiolysis of ether in both phases should be dose-rate dependent. Future work in this respect would be a good test of the mechanisms.

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